

CRYSTALLINE STRUCTURE AND  
CHEMICAL CONSTITUTION



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# CRYSTALLINE STRUCTURE AND CHEMICAL CONSTITUTION

BY

A. E. H. TUTTON

D Sc., M.A. (OXON), F R S., A R C Sc. (LOND.)

*Vice-President of the Mineralogical Society, Member of the  
Councils of the Chemical Society and the British  
Association for the Advancement of Science*

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## PREFACE

THIS memoir has been written in response to a request by the Editor of the series in which it appears for a short monograph, which, with a brief historical introduction, should present in a concise manner the author's original contributions to the subject of the relation between the form, structure, and physical properties of crystals on the one hand, and the chemical composition of the substances composing them on the other. The author has taken the opportunity of bringing together the results of investigations concerning this subject carried out by him during the last twenty years, and published in numerous memoirs in the *Philosophical Transactions* and the *Proceedings of the Royal Society*, the *Journal of the Chemical Society*, and the *Zeitschrift für Krystallographie*. It is hoped that this compilation of a connected story of these researches, and of a concise but comprehensive presentation of their main results, which is always a wise thing to make at that stage of a long series of investigations when definite general results have been arrived at, will be of use to fellow-workers. At the same time, an attempt has been made to present the story in a form which may not be without interest to a much larger circle of readers,

## PREFACE

attracted to a subject ever so fascinating as that of crystals.

The original work to which the volume refers consists of three distinct parts, namely, the devising of new instruments of research, which was necessary in order to raise experimental work in this subject to a high level, the perfection of the means of preparing crystals for research, and the actual measurements of crystal angles and of numerous morphological, optical, and other physical constants. Considerable space has been devoted to the description of the first part, inasmuch as it has become increasingly evident that several of these instruments, notably the interferometer, have wider applications than those immediately connected with the object for which they were first constructed.

It has not been found possible to include within the scope of this book the full historical and contemporary references which the author would have wished to have made, but such omissions will be found remedied in his larger work on *Crystallography and Practical Crystal Measurement*, to be issued by the publishers of the present volume.

The author desires to record his thanks to the Councils of the Royal and Chemical Societies for their kindness in permitting the reproductions of several figures with which the original memoirs were illustrated.

A. E. H. TUTTON.

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# CRYSTALLINE STRUCTURE AND CHEMICAL CONSTITUTION

## CHAPTER I

### INTRODUCTION.

A GREAT scientific *renaissance*, even for times which will be for ever renowned for great advances in natural knowledge, has marked the close of the nineteenth century and the opening of the twentieth. It is generally associated in the popular mind with such remarkable achievements as the terrestrial discovery of the gaseous element helium, and of the other new inert elementary gases of the atmosphere—neon, argon, krypton and zenon ; with the experimental production of electromagnetic ethereal waves and their utilisation for wireless telegraphy ; with the discovery of corpuscles smaller than the chemical atoms, in the cathode rays of the Crookes high-vacuum tube, and of the surprising X-rays secondarily derived from them ; and with the still more wonderful discovery of the spontaneous evolution of both kinds of rays, and of helium atoms and those of another of the inert gases, from uranium and thorium, the two heaviest metals known to us, culminating with the finding of their yet more disintegratingly active relative radium ; together with all the immense consequences which the opening up of this new ultra-atomic world entails.

But concurrently with these achievements, which appeal so powerfully to the imagination, progress of a no less important character, although not so sensational to the public mind, has been made in our knowledge of the nature of crystals, the most perfectly organised and constructed form of solid matter, and of the relations which it has all along been felt must hold between their geometrical forms and their internal structure on the one hand, and the chemical composition of the substances of which they are composed on the other. So late as the year 1890, we were groping in the dark for a fully satisfactory means of accounting for the 32 types of symmetry which crystals had long been known to display. We were not even sure whether any definite chemical substance had its own distinctive crystalline form, for there were no perfectly trustworthy *data* to enable us to fix the precise meaning of the term "isomorphous," invented by Mitscherlich so long ago as the year 1821 to designate the similar crystals of the most closely related chemical compounds; and it was obvious that if the term were rigidly applied, it meant identity of form in the case of a whole series of different chemical substances. Moreover, assuming even that identity were not a fact, and that to this extent the term were a misnomer, we had no idea of any relationships among the crystalline forms of the members of such isomorphous groups, analogous to those which had been shown by Mendeléeff and Lothar Meyer to characterise the other properties of the compounds of the same interchangeable elements belonging to a family group which form the series.

Innumerable isolated measurements and facts had been accumulated concerning the crystalline forms of many unrelated chemical substances, and a few so-called morphoscopic relationships had been pointed out by earnest workers such as Groth. But the position of practical crystallography in the year 1890 was simply one of utter

chaos ; myriads of facts existed without any apparent connection ; and facts, moreover, which were frequently mere approximations, owing to the rough and ready manner in which they had been experimentally derived. In particular did this apply to the optical constants, the methods of determining which were often of the crudest description.

In order to see how great has been the progress, it is only necessary to exercise the reader's privilege of turning at once to the last chapter of this book, as one is so often tempted to do when reading a work of fiction, in order to see what the *dénouement* is going to be ; a *résumé* will there be found of a few of the main results that have been achieved during the interval between the year 1890 and the present time. After perusing that remarkable record, the reader cannot fail to be impressed with the immense advance which it reveals. It has been the author's privilege to assist somewhat in this progress, and the following pages have been written in response to a request to present the story of his contribution in a complete and connected manner, which may prove interesting to a wider circle of readers than that for which the various scattered original memoirs were intended. That the story can be as fascinatingly entralling as the actual work itself proved to the author is not to be expected ; but if it should attract even one or two young and enthusiastic seekers after a sphere of research to *make first a profound study of the present position of the subject*, and then to throw their whole energies into carrying it further forward, the author's temerity in writing it will be fully justified, and he can safely promise to these ardent spirits that they will be entering a field full of the loveliest flowers of nature. For a crystal is to the inorganic world what an exquisite flower is to the organic.

## CHAPTER II

### THE HAUY-MITSCHERLICH CONTROVERSY. ESTABLISHMENT OF THE TYPES OF HOMOGENEOUS CRYSTAL STRUCTURES.

BESIDES the fundamental principles of crystalline symmetry and the law of rational indices, the father of our science of crystallography, the Abbé René Just Haüy, bequeathed to us another great truth, announced by him in the midst of the French Revolution, in the first year of the nineteenth century, namely, that *to every specific substance of definite chemical composition capable of existing in the solid condition there appertains a crystalline form peculiar to and characteristic of that substance.* This principle was, however, for many long years thereafter stubbornly contested, and Haüy was obliged to contend for it with all his energy during the later years of his life. For in 1821 there arose a second great master-mind on the other side of the Rhine, devoted to the chemical side of crystallography as Haüy had been to the geometrical side—Eilhardt Mitscherlich, a profound Eastern scholar as well as a brilliant chemist. His discovery of the similarity of form of closely related substances, such as the phosphates and arsenates, and the sulphates and selenates, of which latter he was the discoverer, led him to propound his great principle of “isomorphism.” There can be no doubt that during the earlier part of his career Mitscherlich really believed that the crystals of each such series of closely related substances, formed by the interchange of similarly-behaving chemical elements belonging to the same family group, actually

possessed complete identity of form. Hence, there arose between Hauy and Mitscherlich and their schools of thought a long controversy, over the apparently conflicting nature of these two great principles. This controversy is now happily settled and the two schools reconciled—both having been proved largely correct—by the results of the researches to be described in these pages.

The question remained much as it was left by Hauy and Mitscherlich right up to the year 1890, when the author commenced his systematic investigations. Many new facts had come to light, however, even in their day. For instance, Wollaston's assertion, based on the measurements made in 1812 with his first reflecting goniometer, that the crystal angles of the carbonates and sulphates of barium, strontium, and lead showed slight differences although their forms were similar, was rejected by Mitscherlich until the results were independently confirmed by Biot. Then Mitscherlich himself showed from his own measurements that small differences do exist in these and many other cases of isomorphism, so that it is clear that Mitscherlich in his mature years gave a wider interpretation to the term "isomorphous" than during the course of his earlier work. But in spite of his construction of a goniometer reading to ten seconds of arc, Mitscherlich still regarded the subject more from the broad standpoint than from the detailed exact one, largely because he was diverted from the field of highly accurate measurement of the crystal angles of isomorphous salts by his work on the thermal expansion of crystals; and he never afterwards

lich broke down at once in the case of the ammonium salts, which are undoubtedly isomorphous, in Mitscherlich's broad sense, with the potassium salts. Moreover, equality in number of atoms is also a false guide in another respect, for it would admit cases like sodium nitrate,  $\text{NaNO}_3$ , and calcite,  $\text{CaCO}_3$ , which are both rhombohedral, and overgrowths of the former on the latter can readily be obtained ; yet they are not chemically similar.

A decisive proof of this lack of true isomorphism in such cases has lately been afforded by the observation of S. Kreutz,<sup>1</sup> working in the University laboratory at Oxford, that barytocalcite,  $\text{BaCa}(\text{CO}_3)_2$ , which is monoclinic in symmetry and not rhombohedral, but has structural constants and a molecular volume very similar to those of sodium nitrate, also permits overgrowths of sodium nitrate to be deposited upon it, indicating that the formation of overgrowths is a question of congruence of the structural-dimensions of the crystal units rather than of the symmetry. Consequently the meaning of "isomorphism" cannot be stretched beyond the inclusion of such similarly crystallising substances, as regards symmetry and observed forms, as are truly chemically similar, the series being formed by members of the same family group of chemical elements, or by radicles such as the ammonium group  $\text{NH}_4$ , which are capable of replacing those elements without altering, in Mitscherlich's broad sense, the crystalline form, and therefore obviously without altering the crystal system and class. The true detailed meaning and ultimate refinement of the law of isomorphism will be brought out fully in later chapters.

During the period which followed the last of the crystallographic investigations of Mitscherlich, new isomorphous series of salts, as also many dimorphous and even polymorphous substances, were discovered in an unceasing flow as

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<sup>1</sup> *Min. Mag.*, 1909, vol. 15, p. 232.

chemistry progressed at the rapid rate for which the nineteenth century will ever be noted. But no further real progress was made with regard to the question of the minute differences which were recorded as being from time to time observed between the angles of similarly crystallising isomorphous substances. Indeed, so irregular did most of these results appear—bearing usually no relation whatever to the atomic weights and chemical order of the interchangeable constituents, and varying considerably among themselves when measured either by different observers or at separate times, and on crystals derived from distinct preparations—that the differences recorded for the same substance in these varying circumstances often exceeded the differences recorded as occurring between two different members of the same series; hence, no definite conclusion was possible, and if any had been drawn it could not have been regarded as trustworthy. Indeed, it was only possible to say that such differences as in reality existed were within the limits of experimental error. Thus the subject remained practically as Mitscherlich left it until the year 1890.

So far as the evidence went, therefore, there appeared to be a direct contradiction between the conclusion of Hauy that difference of crystalline form in general accompanies difference of chemical composition, and the principle of isomorphism as given to us by the masterly labours of Mitscherlich. But it will be shown in the sequel that both were substantially right, as the result of conscientious work, loyal to all the observed facts, always must be, although these facts may have been regarded from a totally different standpoint. And nothing has given the author of this book more real delight than to have been the means of showing, by very materially narrowing the limits of experimental error, that this is truly the case in this instance, and of thus reconciling the work of these two great minds. Indeed, Hauy and

Mitscherlich are typical of the two aspects of crystallography, the geometrical and structural on the one hand and the chemico-physical on the other, aspects which are the natural complement of each other, and together tell us the whole well-balanced story of the nature of crystals.

The geometrical side of crystallography has received a great development, however, contemporaneously with the author's work on the chemical side. It is not the purpose of this book to recount more than the final result of this structural work, as its intention is to describe the progress of chemical crystallography, and mainly that for which the author himself is responsible. But a full account, in historical sequence, will be found in his book on *Crystallography and Practical Crystal Measurement*, shortly to be published by Messrs. Macmillan.

The main points of this geometrical advance are as follows: In the first place the mode of describing crystals, in their seven systems and thirty-two classes or subdivisions of the systems—cubic, tetragonal, hexagonal, trigonal, rhombic, monoclinic, and triclinic—is based upon the clear recognition of the only true elements of symmetry, namely, planes and axes of symmetry, the latter being of two-fold or digonal, three-fold or trigonal, four-fold or tetragonal, and six-fold or hexagonal character. The ideas of hemihedrism and tetartohedrism—the suppression of half or three-quarters of the full number of faces possible to a system, in the classes of the system which exhibit less than the full symmetry—are now altogether discarded. Instead, these classes are merely regarded as possessing a lower number of the elements of symmetry, while the latter is still of the type characteristic of the system. Hence descriptive crystallography has been placed upon a vastly more scientific basis. The greater part of this advance is due to Von Lang and Maskelyne.

In the second place, the geometrical work of Bravais, Schönlies, von Fedorow, and particularly of

Barlow, has established the fact that there are 230, and only 230, types of homogeneous structures, assemblages of similar parts, possible to crystalline structures, and that all of them fall into the 32 classes of crystals. For the essence of a crystal is that it is a homogeneous structure. These 230 structures include the 65 Sohncke regular point-systems, and 165 other structures involving the principle of mirror-image or opposite-wise orientated symmetry.

The 14 space-lattices of Bravais are the foundation of the structure, and comprise all cases of same-way orientated homogeneity. Sohncke's 65 point-systems express the number of ways in which identical repetition can occur, the points being symmetrically and identically arranged about axes of symmetry, sometimes spirally about screw axes. The points may be grouped in sets, the centres of gravity of which form a Bravais space-lattice; so that a Sohnckian system consists in general of two or more interpenetrating space-lattices Schönflies, von Fedorow, and Barlow widened the definition of homogeneity to include "enantiomorphous" similarity, that of a right-hand to a left-hand glove. For to each Sohnckian system not identical with its own mirror-image there corresponds another enantiomorphously symmetrical with it, and the various modes of combining the two, including interpenetration, afford the additional 165 point-systems.

Speaking broadly, the geometrical and chemical sides are connected by the interesting fact that it is the space-lattice which both determines the crystal system and represents the type of edifice built up by the chemical molecules; for the points taken analogously in the molecules, one to represent each, are those which build up the space-lattice. Also it is the configuration (stereometric arrangement) of the atoms in the molecule that largely determines to which particular one of the 230 types of homogeneous structures, and therefore to which of the 32 classes of symmetry, the crystal shall conform.

## CHAPTER III

THE INFLUENCE OF THE PERIODIC GENERALISATION. MEMOIR  
(1884) EXPLAINING IT BY, AND ASSERTING, THE COM-  
POSITE NATURE OF THE ATOM.

A PROFOUND influence has been exercised on chemistry and its allied subjects by the discovery by Newlands in the year 1863, that when the chemical elements are arranged in the arithmetical order of their atomic weights, they exhibit a periodically recurring sequence of properties, which, as the recurrence happens after every seventh element (leaving out of consideration certain transitional elements which occur after every fourteenth element), he called the “Law of Octaves”; for the seven elements form a series or period corresponding obviously to the seven major notes in the musical octave. It is, indeed, extraordinary how frequently the number seven possesses a special significance in nature, and the seven systems of crystal architecture will at once come to the mind as another example *à propos* to the subject of this book.

The periodic table of the elements of Newlands was perfected in its details in the year 1869 by Mendeléeff, who also directed attention to the transitional elements of the eighth group, which occur in the even series beginning with the fourth. In subsequent memoirs also, including the Faraday lecture to the Chemical Society in the year 1889, Mendeléeff further elaborated the meaning of his table, and placed the “Periodic Law of the Elements,” as it has now come to be universally called, on a sure and

firm foundation. The generalisation is now so well known that it will be quite superfluous to do more here than to recall its main conclusion, namely, that :

*The whole of the properties of the chemical elements, both chemical and physical, are periodic functions of their atomic weights.*

The table on page 12,—which has been most carefully brought up to date so far as trustworthy atomic weight determinations and work on new and rare elements are concerned, including the insertion of the inert atmospheric gases discovered by Sir William Ramsay,—will remind the reader as to the character of the periodic classification. The series of seven elements belonging to each period are arranged in a horizontal row, and each such series is one growing in valency, and passing from electro-positive, through neutral, to electro-negative character. The recurrence after every seventh element (omitting the transitional and inert gaseous elements of the eighth group) causes the several series to be set vertically under each other, and thus the formation of a number of vertical family groups of elements having similar properties, but not identical ones; a steady progression in the properties of the members of the vertical family groups is indeed just as evident as in the horizontal series, although now in the direction of increase of electro-positive or decrease of electro-negative chemical affinity, the valency remaining the same. Lothar Meyer assisted largely in working out the periodicity of the physical properties of the elements, and the results of his labours placed the physical side of the subject on an equally sound basis of fact.

The greatest of all the valuable influences of this generalisation was the stimulus to thought concerning the nature and origin of the chemical elements to which it gave rise. The author's first contribution to original science consisted in a paper read on May 2, 1884, to the Debating Society of the Normal School of Science and

THE PERIODIC CLASSIFICATION OF THE ELEMENTS.

Period No.	FAMILY GROUPS									
	I	II	III	IV	V	VI	VII	VIII		
	R <sub>2</sub> O	R <sub>2</sub> O <sub>2</sub>	R <sub>2</sub> O <sub>3</sub>	R <sub>2</sub> O <sub>4</sub>	R <sub>2</sub> O <sub>5</sub>	R <sub>2</sub> O <sub>6</sub>	R <sub>2</sub> O <sub>7</sub>	R <sub>2</sub> O <sub>8</sub>		
1	$\frac{1.068}{H=1.000}$	$\frac{Li=6.98}{Li=6.98}$	$Be=9.08$	$B=10.9$	$C=11.91$	$O=15.88$	$P=18.9$	$I_0$		
2	$Mg=22.88$	$Mg=24.18$	$Al=26.9$	$Si=28.2$	$P=30.77$	$S=31.32$	$Cl=31.18$	$He=19.9$		
3	$K=38.85$	$K=39.10$	$Ca=39.7$	$Sc=43.8$	$Ti=47.7$	$V=50.8$	$Cr=51.7$	$He=20.0$		
4	$Ge=63.1$	$Ge=64.9$	$Ge=65.9$	$Ge=67.5$	$As=74.4$	$As=74.4$	$Se=75.0$	$He=21.1$		
5	$Rb=84.0$	$Rb=85.45$	$Sn=84.9$	$Sn=85.62$	$Yt=88.3$	$Zr=89.9$	$Sc=78.0$	$He=22.1$		
6	$Ag=107.88$	$Ag=107.11$	$Cd=111.6$	$Cd=112.10$	$In=114.1$	$Sn=115.1$	$Sn=119.3$	$He=23.1$		
7	$Cs=131.9$	$Cs=131.81$	$Ba=136.4$	$Ba=137.37$				$He=24.1$		
8					$Yb=170.7$	$Yb=170.7$	$Ta=170.6$	$He=25.1$		
9								$He=26.1$		
10								$He=27.1$		
11	$Au=197.2$	$Au=195.7$	$Hg=198.5$	$Hg=200.0$	$Tl=202.6$	$Pb=203.35$	$Bi=206.4$	$He=28.1$		
12					$Ra=225.7$	$Th=230.8$	$U=236.7$	$He=29.1$		

The atomic weights in ordinary figures are those authorised by the International Committee on Atomic weight, 1905, for hydrogen=1, corrected and brought up to date (1916) as regards trustworthy determinations which have since been made. The figures in type are on the basis of O=16, as authorised by the International Committee in February, 1909. No elements of doubtful position have been inserted in the table.

Royal School of Mines, South Kensington, on "The Evolution of Matter," and this was subsequently brought up to date in a further paper, entitled "The New Atomic Theory," which was read to the same Society on November 19, 1886, and published in the then recently inaugurated *Science Schools Journal* for January 1887, the magazine of the above named Institution at South Kensington, since known as the Royal College of Science. The ideas in both these papers concerning the possibility of a common source for all the elements, and of a process of evolution by which they might be successively formed from that primary or protylian substance, were much on the lines which were so ably advocated and elaborated by Sir William Crookes in his epoch-making address to the Chemical Section of the British Association at their 1886 meeting in Birmingham, and in his subsequent lecture at the Royal Institution on February 18, 1887. At the time of the author's 1884 paper—the original MS. of which is now before him, very many of the bold predictions and suggestions in which are now proved facts—he was quite unacquainted with the views of Sir William Crookes, but his 1886 paper was largely influenced by them.

It is both highly interesting and instructive that the ideas at that time put forward should now be in process of realisation and, indeed, largely actually realised. For the experimental discovery, by Sir J. J. Thomson and his school of workers, of the composite nature of the atom, of its constitution by the electronic-corpuscles, and of the gradual development of the atoms of one element after another by further and further accretions of corpuscles in cycles or groups, has shown that these views, regarded at the time as so wild and revolutionary, were not far beside the mark. The author well recalls the good-natured ridicule which his opinions, expressed in the 1884 paper, called forth from his fellow students, banter which was excellently expressed by one of them, Mr. H. G. Wells, who at

that time already exhibited the literary talent for which he has since become famous, in a poem in the succeeding number (February 1887) of the *Science Schools Journal*, entitled "Protylean Vapourings." It may not be without interest to quote the first part of the concluding paragraph of this 1884 paper of the author, which runs as follows :—

"The relations which we have pointed out between the elementary forms of matter, and embodied in Newland's 'Law of Octaves,' seem to be fully explained by assuming that the difference is due to the different amounts of primary matter contained in each so-called atom. Thus, as we are pretty certain that hydrogen is not primary matter, let us say that an atom of hydrogen contains  $x$  primary particles or atoms, held together by their inertia of revolution, then our theory says that sodium contains  $23x$  primary atoms ; consequently the ring must be more closely packed, and less energy can be externally manifested. Similarly, potassium has  $39x$  primary particles to the atom, and mercury  $200x$  primary particles "

If for " $x$  particles of primary matter" we read " $x$  electronic-corpuscles" the above is at once translated into actual fact, as we now know it.

These early studies of the author left a very deep impression on his mind as to the progressive evolutionary effect of accretions of the primordial matter, which we know now in real truth as the electronic corpuscles, the same which are set free in the "cathode rays" of the high-vacuum Crookes tube, and are also spontaneously evolved as the  $\beta$ -rays by the wonderful new metal, radium, and radio-active substances in general. It is now proved that from whatever source these  $\beta$ -corpuscles are derived they always have approximately the same mass, about the one-thousandth part of the mass of an atom of hydrogen, the element of lowest atomic weight. This latter is retained as unity in the table given on page 12, although it has lately become the fashion to take oxygen as the standard at 16.00, when hydrogen becomes 1.008 ; the latter is a course which has some advantages but, in the author's opinion, and until an element is discovered of lower atomic weight than hydrogen, also more disadvantages.

The atomic weights referred to oxygen as 16 are, however, also given in the table in italics.

It was obvious that the assumption of such an effect, due to successive accretions of cycles of corpuscles, fully explained the progressive nature and the chemical and physical properties of the atoms of the chemical elements; and that it was likely that this different nature, as exhibited most strikingly of all by the difference in the property known as atomic weight, would be carried through to every property whatsoever. Hence, when the author took up his special line of research—the relations of chemical constitution to crystalline form—he was quite prepared to find this effect exhibited in the properties of the crystals of isomorphous series, formed by interchange of the members of the vertical family groups of elements, just as in all other physical properties; and this led him to choose, as the most favourable group to show the relationships well, the most electro-positive group of all—that of the alkali metals.

## CHAPTER IV

### INVESTIGATIONS OF ISOMORPHOUS SERIES.

THE chemico-crystallographical position in the year 1890, when the author commenced a systematic series of investigations, has been fully set forth in the first two chapters, and the following explanatory statement, made at the commencement of the memoir in 1893,<sup>1</sup> describing the first series of measurements, the results of three years' work, expresses the author's object in clear terms.

"The direction in which pure crystallographic research appears likely to afford results of the greatest interest and significance is that in which comparable measurements are made upon crystals of substances chemically related to each other in a definitely ascertained manner. The information at present (1893) available, particularly with regard to the goniometrical effect produced by the replacement of one metal in an isomorphous series of salts by another, is of the most meagre and insufficient character. The absence of conclusive data is, however, largely accounted for by the fact that, especially in the cases of substances crystallising in the higher systems of symmetry, the values of analogous angles upon the crystals of the various members of the series are so nearly identical that the differences frequently fall within the limits of the few minutes usually assigned to experimental and formational error."

The object of this first investigation was to examine in great detail some well defined but hitherto unattacked series of isomorphous salts crystallising in one of the systems of lesser symmetry, with the view of ascertaining whether the replacement of one metal by another of the same family group but of higher atomic weight were attended by a change in the values of the angles of sufficient magnitude

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<sup>1</sup> *Journ. Chem. Soc. Trans.*, 1893, 63, 337; and *Zeitschr. fur Kryst.*, 1893, 21, 491.

to be far removed from the narrow limits (not more than 3' or 4') of experimental and formational error. The attention of the author was at once attracted to the well known series of double sulphates crystallising in the monoclinic system with six molecules of water, of which potassium magnesium sulphate  $K_2Mg(SO_4)_2 \cdot 6H_2O$  may be considered as the first member. Measurements, not, however, sufficiently numerous and detailed for the purposes of this investigation, had already been made of the potassium and ammonium salts of this series by several crystallographers, notably Brooke, Rammelsberg, and Murnmann and Rotter. The salts containing rubidium and caesium, however, first prepared by Bunsen, which are more directly comparable with those containing potassium than are the salts of ammonium, had never been measured, and as these three metals—potassium, rubidium, and caesium—form the most electro-positive family group of the periodic classification of the elements, to which reference was made in the last chapter, the crystals of their salts might be expected to exhibit any angular and physical differences at a maximum. It was decided, therefore, to prepare crystals, as suitable and perfect as possible, of all the salts of the series containing potassium, rubidium, and caesium, and to subject them to a goniometrical investigation as complete as their development would permit.

On making a comparison of the angular values given by previous observers for the salts of this series,  $R_2M(SO_4)_2 \cdot 6H_2O$ , in which R is potassium and M is magnesium, zinc, iron, nickel, cobalt, and copper, no regular differences were observed. In a large majority of cases the differences were small, and where larger they exhibited no relationship to the atomic weights of the dyad metals (or acting dyads) contained. Moreover, in the case of one and the same salt, the differences in the values of the angles given by different observers frequently amounted to half a degree, thus vitiating any possible comparison. These

discrepancies were probably due partly to the fact that a sufficient number of measurements had not been made upon different crystals belonging to separate crops, and that the crystals had not been grown under sufficiently perfect conditions for absence of disturbance during growth.

In the work now to be described, therefore, at least ten crystals were selected on account of their special perfection and suitability as regards size, small ones being generally preferable, from as many crops as possible, in order that all such differences as have just been referred to might be eliminated, when the mean results were taken of all values derived from faces yielding perfect single images of the goniometer signal. Such beautifully perfect crystals of most of the salts have been eventually obtained, by working under the most favourable conditions for slow undisturbed growth, that these differences in the values of the angles of one and the same salt have been reduced to very small proportions, far smaller than those above mentioned as being shown by the work of previous observers.

The work described in the 1893 memoir on the double sulphates (*loc. cit.*) included the results of the goniometrical investigation of 22 salts of the series, namely, those in which R is potassium, rubidium and caesium, and M is magnesium, zinc, iron, nickel, cobalt, copper, manganese and cadmium. The number of salts should obviously be 24, composed of eight sets, each consisting of three salts containing the same dyad metal but a different alkali metal. But two were found to be incapable of preparation, namely, potassium manganese and potassium cadmium sulphates. The results, which will be fully discussed in later chapters, proved so interesting that it was felt that the investigation should be largely extended, and should not only include the determination of the whole of the physical properties of the crystals of

these same substances, but that the ammonium and thallium salts of the series should be included. Further, the results had revealed that the alkali metals played a vastly predominating part in determining the structure of the crystals of these double salts; for while the differences between the potassium, rubidium, and caesium salts of any set proved to be considerable, and subject to a definite law, the effect of replacing the dyad metal by another one was almost inappreciable.

It was, therefore, decided to investigate fully also the simple normal sulphates of the alkali metals themselves,<sup>1</sup> potassium, rubidium, and caesium; and also those of ammonium<sup>2</sup> and thallium,<sup>3</sup> which are capable of replacing the alkali metals proper. This is the rhombic series  $R_2SO_4$ , and its investigation has been carried out in great detail, both goniometrically and physically.

Further, the work of Mitscherlich having shown that the selenates were isomorphous with the sulphates, it was considered advisable to bring the corresponding selenates<sup>4</sup> and double selenates into the scope of the investigation, so that not only the effect of replacing sulphur by selenium in all these salts could be observed, but also that an independent series of results should be afforded for the effect of the replacement of one alkali metal by another or by ammonium or thallium. The possible argument that the results with one series might be merely fortuitous would thus be met and disproved, if it were found that perfectly parallel results, each pointing to the same conclusions, were obtained for the two series.

The results of all these investigations, or rather these several parts of one broad and clearly pre-determined investigation, have been communicated to the Royal and

<sup>1</sup> *Journ. Chem. Soc.*, 1894, **65**, 628.

<sup>2</sup> *Ibid.*, 1903, **83**, 1049.

<sup>3</sup> *Proc. Roy. Soc.*, 1907, **79**, 351.

<sup>4</sup> *Journ. Chem. Soc.*, 1897, **71**, 846, and 1906, **89**, 1059.

Chemical Societies in a series of memoirs, the references to which are given in the accompanying footnotes. The work on the simple sulphates and selenates  $R_2\overset{S}{\text{Se}}\overset{O_4}{\text{O}_4}$ , has been completed, and includes ten salts, those of potassium, rubidium, caesium, ammonium, and thallium. They have been investigated in great detail goniometrically and as regards their volumes, solubilities, optical properties, and—in the cases of the sulphates of potassium, rubidium, and caesium—their thermal expansion.<sup>1</sup>

As concerns the double sulphate and selenate series,  $R_2M\left(\overset{S}{\text{Se}}\overset{O_4}{\text{O}_4}\right)_2 \cdot 6\text{H}_2\text{O}$ , the 22 salts containing potassium, rubidium and caesium, referred to as being described goniometrically in the 1893 memoir, were completed subsequently in the year 1896 with respect to their optical and other physical properties.<sup>2</sup> Next, the six corresponding double selenates containing the same three alkali metals, and zinc and magnesium respectively as the dyad M-metal, were studied both goniometrically and physically and described in 1900 and 1901.<sup>3</sup> Four ammonium salts of the series, ammonium magnesium and ammonium zinc sulphates and selenates, were then completely investigated, and the results published in 1905.<sup>4</sup> Lastly, coming right up to date, two typical thallium salts of the series, thallium zinc sulphate and selenate, have been similarly worked out in full detail. Hence, one complete set of ten salts, double sulphates and double selenates in which zinc is the M-metal, have been investigated, and this set of ten salts may be taken as a typical example of the eight sets of the series, containing respectively the eight M-metals which are

<sup>1</sup> *Phil. Trans.*, 1899, A, 192, 455.

<sup>2</sup> *Journ. Chem. Soc.*, 1896, 69, 495.

<sup>3</sup> *Proc. Roy. Soc.*, 1900, 66, 248 and 67, 58; *Phil. Trans.* 1901, A, 197, 255.

<sup>4</sup> *Journ. Chem. Soc.*, 1905, 87, 1123.

capable of replacing one another in the series. Besides these ten, 34 other salts of this series have thus been examined, making 44 in all. Adding these to the ten simple salts, we arrive at the total of 54 salts investigated up to date.

Probably practically all the principles to be derived from the investigation have now been learned, for it is found that the different sets behave so similarly that it is even possible now to prophesy beforehand, with some considerable accuracy, what their angles and physical constants will be, so definite are the laws which have been discovered to hold throughout. Indeed this has actually been done for the two double sulphates of the series containing potassium as the R-metal and manganese and cadmium respectively as the M-metal, which have already been mentioned as not having yet been successfully prepared. Although this is so, the author is steadily progressing with the complete experimental working out of the whole series, which he trusts to be able to leave completely investigated. For in spite of the broad similarity of the sets just mentioned, one of the most remarkable facts brought to light is the difference in detail, particularly in the optics, exhibited by the various sets; for although they all show the same comparative facts, they each do so in their own particular way, thus affording so many independent and highly valuable confirmations of the principles derived as the main conclusions from the whole work.

It will be apparent that the labour involved in preparing a very large number of crops of each of these 54 salts, for the purpose of studying every variety of habit which they develop under different conditions, and from materials of the utmost refinement of purity, tested both by quantitative analysis and spectroscopic examination, has been very great, quite apart from the actual investigation of the selected crystals themselves. They were all grown under

such conditions of protection from mechanical and thermal disturbance as had probably never before been attempted. Moreover, special precautions had to be taken from the outset to avoid the development on the crystals of the highly interesting, but for our purpose most disconcerting, vicinal-faces, faces of very high indices, which have been studied by H. A. Miers<sup>1</sup> and which, under certain conditions which the author sought to avoid and succeeded in avoiding, tend to replace the normal faces of simple indices.

As regards the operations involved in the actual investigation of the selected crystals, never fewer than ten and often more small crystals of high perfection were selected for the goniometrical work from among as many as fifty or even occasionally a hundred crops. Their interfacial angles were measured on the best of goniometers, an instrument constructed by Fuess (No. 2a), which had been verified throughout its whole circle to afford absolutely trustworthy readings. Over 25,000 different angles have been measured in all. The optical investigation has included the determination of the orientation of the optical ellipsoid in all cases (the monoclinic salts) where it was not fixed by the symmetry, the measurement of the refractive indices, and of the optic axial angles, usually with the aid of over a dozen different crystals of each substance, larger than those used in the goniometry. Moreover, all such measurements have been made for at least six different wavelengths of light, taken at suitable intervals along the spectrum; and the observations have been repeated at temperatures up to 100° C., in order that the results should be free from the imputation of representing a single (the ordinary) temperature only, and so that any fundamental conclusions should thus be independent of the temperature.

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<sup>1</sup> *Phil. Trans.*, 1903, A, 202, 459.

For this optical work as many as 400 section-plates and an equal number of  $60^\circ$ -prisms have been cut or ground out of the crystals, accurately orientated to within two or three minutes of arc, as required ideally by theory, but never before achieved. Specially designed instruments for this purpose, and for the production of monochromatic light of any or every wave-length, have been devised and constructed for the purpose of this work, and these instruments will be described in the next two chapters.

Further, an entirely new interference dilatometer, based on Fizeau's principle, but of quite different construction and much more convenient for crystal work, has been employed for the determination of the thermal expansion of the rhombic crystals of the simple sulphates of potassium, rubidium, and caesium ; and the interferometer devised specially for this instrument has since had important developments, being found suitable for fine measurement in general, to the degree of fineness of the one eight-millionth of an inch. This instrument and the dilatometer will be described in Chapters VII. and VIII.

Perhaps one of the most valuable portions of this work, however, has been the investigation of the volumes of all these substances. For all of them have had their densities determined in the most accurate manner which it has been possible to devise, the suspension method of Retgers having been rendered still more accurate for the purpose ; and where it was not applicable, owing to the high density of the substance being superior to the specific gravity of any available immersion liquid, an extremely refined modification of the pyknometer method has been used instead. Indeed, in most cases of lower density, both methods have been employed. The results have not only enabled the molecular volumes to be calculated, but, owing to the development, by Muthmann and the author, simultaneously and independently, of the new and highly fruitful idea of "molecular distance ratios" as the author

calls them, or "topic axial ratios" as they are termed by Muthmann, it has been possible actually to determine the relative dimensions of the elementary parallelepipeda of the space-lattice of the crystal structure. So important, indeed, has this portion of the work become, that a special chapter will be devoted to the discussion of it.

The foregoing will have given some idea of the scope of the investigations, and reference may now be made to some of the details of the work which are of general interest, involving new principles or new experimental methods, after which the results themselves will be briefly summarised. It will be convenient to state the latter under two distinct heads, those for the rhombic simple sulphates and selenates, and those for the monoclinic double salts. In the former case it is only necessary to compare the ten salts themselves. In the case of the very large monoclinic series, the author proposes to describe the results completely for one set of ten salts, in which the same dyad metal, zinc, is present as the M-metal, and the R-element or radicle is represented by potassium, rubidium, caesium, ammonium, and thallium, thus affording five double sulphates and the corresponding five double selenates, together making up the whole set of ten. This set has now been actually completed, and, as the results are precisely parallel in the cases of all the numerous members of the other sets which have also been investigated, such a typical set will serve as an example of the relations throughout the series

## CHAPTER V

### IMPROVED APPARATUS FOR THE INVESTIGATION OF CRYSTALS. THE CUTTING AND GRINDING GONIOMETER.

BEFORE the investigation of the crystals of the two series could be undertaken with any hope of bringing the determination of the physical constants to anything like the accuracy of the measurement of the goniometrical angles, it was absolutely necessary that a whole battery of new instruments should be devised. The determination of the refractive indices, and of the optic axial angles with a high degree of accuracy had been rendered possible by the construction of the No. 1a Fuess goniometer-spectrometer—an admirable instrument reading to seconds of arc, and with an error not exceeding a very few seconds,—and of the larger optic axial angle goniometer also placed at the disposal of crystallographers by Fuess of Berlin. But for their use it was essential that  $60^{\circ}$ -prisms and parallel sided section-plates should be cut or ground out of the crystals. For the refractive index is best determined with the aid of a  $60^{\circ}$ -prism, and if the crystal belongs to any system other than the cubic, the prism should be cut in an accurately orientated direction with respect to the crystal faces, so as to afford two indices directly. A single such prism suffices if the crystal is tetragonal, hexagonal, or trigonal, provided the refracting edge is made either parallel to the optic axis, the principal axis of the crystal, or perpendicular thereto, and the bisecting plane in the latter case parallel to the optic axis. If the crystal is rhombic, mono-

clinic, or triclinic, two  $60^{\circ}$ -prisms are required, each cut so that its refracting edge is parallel to one of the three rectangular axes of the ellipsoid which represents the optical properties, and so that its bisecting plane is parallel to the plane containing this axis and a second of the three, that is, parallel to a principal plane of the ellipsoid.

Moreover, the orientation of the ellipsoid has to be determined in the case of the last two systems, where the symmetry itself does not fix it, with the aid of a section-plate or section-plates. In the case of a monoclinic crystal the ellipsoid has one of its axes fixed, for it is identical with the symmetry axis perpendicular to the symmetry plane, but it is free to rotate about that axis, and a section plate perpendicular to that axis, and consequently parallel to the symmetry plane, is required for the determination of the direction of the other two axes of the ellipsoid, by the process of determining the directions of extinction in the parallel-light polariscope under crossed nicols. A pair of section-plates are also required perpendicular to two of the axes of the ellipsoid, the first and second median lines or bisectrices of the acute and obtuse angles between the optic axes, for the purpose of determining the optic axial angle, both the apparent angle as seen in air and the true angle of separation of the optic axes in the crystal itself.

Hence, in general, two  $60^{\circ}$ -prisms and three section-plates are required to be cut or ground out of the crystal, and polished truly plane, for the determination of the optical constants. As a good observer, however, is never content with a single determination, duplicates should also be measured, and the author has made an invariable rule of preparing and making determinations with three sets at least, in order to arrive at the probable truth independent of peculiarities of growth shown by any one crop of crystals. Hence, six  $60^{\circ}$ -prisms and nine section-plates of every substance investigated required to be prepared, absolutely truly orientated as regards their directions

within the crystals, and furnished with truly plane, well reflecting and refracting, surfaces.

Now such a task had never previously been undertaken with the relatively soft and very small crystals of artificial salts. Indeed, the scantiness of optical data afforded by the literature of the subject, and the imperfect character of much that was published, was due to this fact of the difficulty, nay, impossibility under the then existing conditions, of preparing such prisms and plates. The only known method was to hold the small crystal between the finger and thumb, and to grind it down on a ground-glass plate moistened with oil, trusting to luck and the skill with which the crystal could be held down in the right direction, to obtain the desired surface. Its position required then to be measured on the goniometer, and as it was invariably, except by the merest chance, found to be considerably out of truth, a second attempt had to be made to correct this. Even when the direction was eventually more or less correctly attained, the surface was almost always slightly curved, and to obtain anything like a correct value for the refractive index or optic axial angle, a small glass plate had to be cemented upon it by balsam, as otherwise no trustworthy image could be obtained from it. Hence, it was essential that an instrument should be devised and constructed, by means of which accurately orientated surfaces could be ground on the crystals in any desired directions and polished truly plane.

Such an instrument was at length perfected, and has proved simply invaluable. As a matter of fact, this research could never have been completed without it, and the results could not possibly have been endowed with the same trustworthy character. It was constructed to the author's designs by Messrs. Troughton and Simms. Indeed, two of these instruments have been constructed, the first of which was intended for use with the relatively soft crystals of artificial salts only, the particular problem confronting the author;

this was consequently only provided with grinding and polishing gear. It proved so successful, however, that it was succeeded by a second instrument constructed on a somewhat larger scale, which could be used with either artificial substances or the harder crystals of natural minerals, and was, therefore, provided in addition with a cutting gear. The two models are equally efficient for their specific purposes, but as the second covers all that the first can do and much more besides, it will be sufficient to describe the larger model. It ought to be stated that no attempt was made at cheapness of construction, for the instrument was solely designed with the idea of carrying out its functions in the most perfectly efficient manner for the purposes of original investigation, quite irrespective of cost. Hence, the price is necessarily high, £80 for the larger model and £50 for the smaller. The larger instrument is shown in Fig. 1, about one-fourth its real size. The author has termed it the "Cutting and Grinding Goniometer," and references to the memoirs describing this and the earlier instrument are given in the footnote.<sup>1</sup>

The instrument consists essentially of four parts, (1) a delicate suspended horizontal-circle goniometer reading to half-minutes of arc, (2) a diamond-wheel cutting gear, (3) a grinding and polishing gear, provided with interchangeable laps of different materials to suit crystals of all grades of hardness, and (4) a sensitive device for varying and controlling the pressure with which the crystal bears on the grinding or polishing lap during action, a very essential and especially successful part of the instrument, for it renders it possible to prepare a surface on the softest and most friable of crystals without danger of fracture or destruction.

The goniometer portion carries all the accessories and conveniences of the best Fuess goniometers, besides

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<sup>1</sup> *Phil. Trans.*, 1895, A, 185, 887; *Proc. Roy. Soc.*, 1895, 57, 324; *Phil. Trans.*, 1899, A, 192, 457.

several additional adjuncts for the special object in view. The chief of the latter are the crystal-adjusting move-

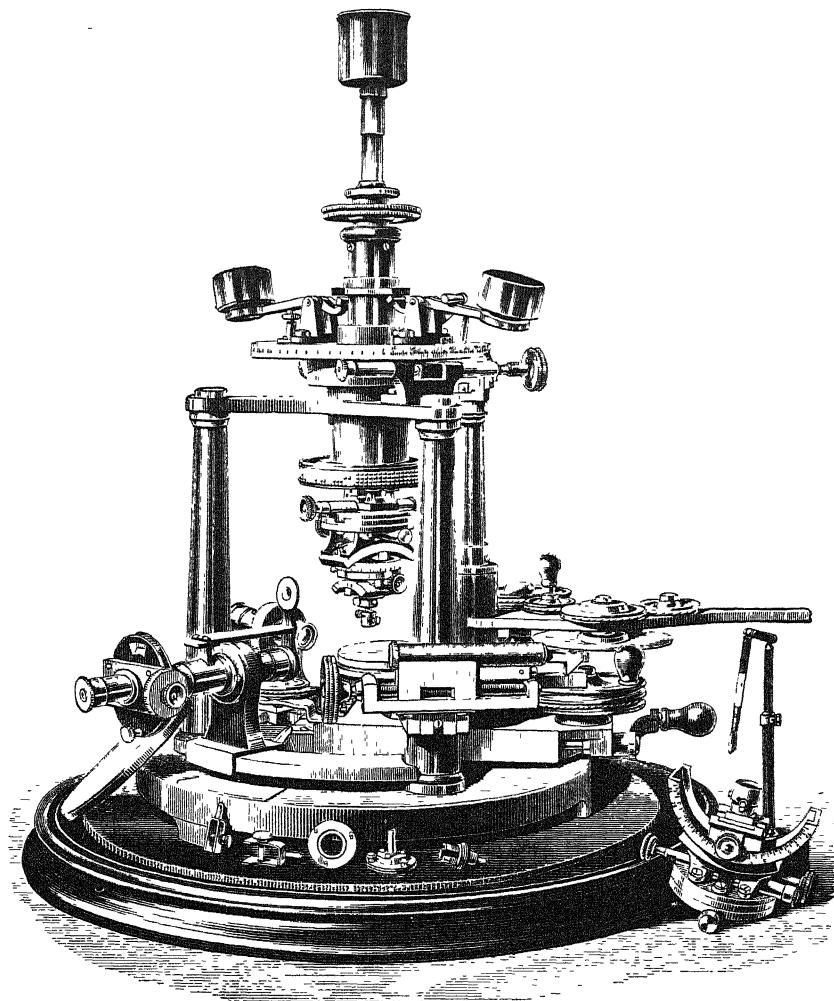


FIG. 1.—THE CUTTING AND GRINDING GONIOMETER

ments, which are given in duplicate, the construction being different in the two cases. Both differ from the ordinary pair of centring and couple of segmental circular

adjusting movements in that the latter (from which the crystal holder is suspended) are graduated, the guiding segments bearing divided silver arcs, and the sliding segments carrying central indicator marks on silver. In the case of the set shown in position in the centre of Fig. 1, a horizontal circle also divided on silver is inserted between the two segmental circular movements, in order that the lower one of the latter can be set at any desired angle to the upper one. In most cases  $90^\circ$  is the proper setting, but the movement about the horizontal circle confers the power of setting the vertical planes of the two circular adjusting movements to any other angle, that of the prism of a triclinic crystal, for instance, if such is considered desirable. This is the set of adjusting movements most suitable for use in preparing section-plates.

The second set of adjusting movements, shown to the right of the baseboard in Fig. 1, is intended for the preparation of  $60^\circ$ -prisms, and differs from the first set in having no intermediate horizontal circle, but instead of the upper cylindrical movement having only a scope of  $35^\circ$  on each side of the centre, which is sufficient for the ordinary purposes of such an adjustment, the possible amount of movement is increased to  $75^\circ$  on each side of the centre, by means of an additional cylindrical arc of somewhat over  $150^\circ$ . This renders the whole adjusting attachment somewhat more cumbrous than that of the first set, but the advantage gained for the specific purpose in question is amply repaying, and the apparatus is detached and replaced by the first set for all other purposes. For in order to prepare, with a single setting of the crystal on the holder, the two refracting surfaces of a  $60^\circ$ -prism, it is obviously necessary to rotate the crystal for  $60^\circ$  on each side of the particular principal plane of the optical ellipsoid which has been adjusted perpendicular to the grinding plane, and which is to be the bisecting plane of the prism. This the second set enables the

manipulator to do with facility. The preliminary adjustment is carried out with the usual upper and lower circular (cylindrical) movements, for the upper one is given as in the first set, independently of the large additional arc which moves just below it concentrically; then, the crystal being fully adjusted so that the plane of the optical ellipsoid in question will be the bisecting plane of the required prism when ground, the special arc is brought into play, and the lower movement with the crystal is rotated first on one side for  $60^\circ$  and a surface prepared, and then on the other side for  $60^\circ$ , when the second surface of the prism is ground and polished. It is a great advantage thus to be able to avoid having to set the crystal twice on the holder for the separate adjustment and grinding of the two surfaces. For not only is much valuable time saved, but the crystal and particularly the first ground surface are protected from possible unnecessary injury.

The crystal is attached to a special form of holder, which is itself capable of a certain amount of circular adjustment about a cylinder and is seen in position at the lower end of the adjusting movements in the figure, by means of hard optician's wax; or it is held in one of several grip-holders shown in the foreground on the baseboard in Fig. 1, and either form of holder with its crystal is suspended underneath the adjusting movements by means of a keyed stem. The goniometer enables the most accurate adjustment to be carried out, so that any desired direction within the crystal may be brought either parallel to or perpendicular to the grinding plane, for sometimes it is convenient to adjust the direction in which a surface is to be ground directly, and at other times the disposition of faces and the development of a suitable zone may render it easier to adjust the perpendicular direction to that along which a surface is to be ground. In any case the movements

provided enable any desired adjustment whatsoever to be readily attained.

The great point of this instrument is that instead of preparing a surface first and then testing it afterwards for truth of direction, it actually sets the true direction first, so that the surface ground cannot then help being true. For no movement of parts is possible, locking screws being fixed as soon as the adjustment is completed. Being itself a perfect goniometer as accurate as any employed for crystal measurement, the truth of surface attained can at once be verified *in situ*, by moving the adjusting segments back to the original readings corresponding to the adjustment of the zone of faces used as starting point, if such a zone is not already left in adjustment for the grinding (as it would be if a plate perpendicular to that zone axis is to be prepared).

The device for modifying the pressure of the crystal on the grinding lap consists in the introduction of an additional axis to the instrument, between the outer circle axis and the inner crystal axis, which can be operated by means of the two counterpoised levers seen above the circle-plate to right and left, and is capable of vertical motion only. The author generally throws one of the counterpoises out of action by means of a screw arranged for the purpose, and manipulates the other with the left hand, while rotating the grinding lap with the right hand. This enables the grinding pressure to be varied from nothing up to the weight of half the axis and all that it carries (crystal adjusting apparatus and shaft); for when both levers are in operation they counterpoise the whole weight of the axis and adjusting movements. The delicacy of this method of working with one lever only is such that by the "feel" of the pressure against the left hand the operator can tell precisely how the grinding is proceeding, and whether the weight on the crystal is approaching the

danger point or is on the safe side of the latter. The author is shown manipulating the instrument in this manner in Fig. 2.

There are ten different interchangeable truly plane laps.



FIG. 2.—GRINDING A CRYSTAL SURFACE.

of various finenesses of ground glass and different metals of various hardness for grinding, and of wood, optician's wax, and polished glass for polishing purposes. Provision is thus made for dealing with crystals of every degree of

hardness. One of the metal laps is shown in position in Fig. 1, and another of glass reared up against the base of the instrument. The lap is rotated in a manner which is practically frictionless, owing to the provision of an extra friction pulley to take up the pressure of the band which would otherwise bear on the axle, on the other side of the lap-pulley to the driving wheel. The whole grinding gear is mounted on a horizontal slide, so that it can be moved about on its dove-tailed bed to prevent any part of the lap becoming unduly worn. The cutting gear is mounted quite separately on an arm, which is pivoted about the back pillar in such a manner as to be rotatable out of the way when grinding or other operations are in progress ; the other end of the arm rests in a fitting about the front pillar, and this is also detachable. It is also furnished with a means of avoiding strain during cutting ; for the directing screw for manipulating the cutting wheel and determining the rate of cutting forms part of the bearing about the front pillar, and it is fitted with a safety spring, which gives way the moment there is danger of too rapid cutting or of jamming. This directing screw with large milled head is intended to be manipulated by the left hand, while rotating the diamond-fed cutting disc with the right hand by means of the driving wheel.

There are numerous time-saving and other convenient accessories, such as an adjustable brush on a stand, shown to the right in Fig. 1, for keeping the lap lubricated with brick oil during the grinding of the crystal, and for sweeping the grinding path free of crystal particles ; and especially a device for grinding a second surface parallel to the one first ground, which avoids the otherwise necessary resetting of the crystal on the holder by the wax and its readjustment.

The latter fitting is of really immense service in preparing section-plates. The crystal is mounted by its first ground surface on a circular glass disc one centimetre in

diameter; a large number of these discs, cut out of parallel plate glass, are kept in stock. The disc is then fitted into a very shallow annular rabbet in a thin metal cap, so that the crystal projects through the 7-millimetre aperture of this cap, when the latter is fitted into position over a stout circular truly plane disc of gunmetal 2 centimetres in diameter, which replaces an ordinary crystal holder. This fits by a central perpendicular stem into the socket bored centrally up into the lower adjusting movement for the reception of the stems of the crystal holders. This true plane is "sighted" truly parallel to the grinding lap once for all; if the stem is truly perpendicular the readings on the two adjusting segments for parallelism of plane and lap should be zero, but, as a matter of fact, they differ a few minutes from this, the amount being determined once for all; as the stem is keyed in the socket, like the stems of all the crystal holders, it always takes up the same position whenever inserted.

It only remains, therefore, to fit the cap with its crystal and glass supporting plate underneath the true plane, to screw it firmly on with three little milled-headed screws supplied for the purpose, and to grind away at the second surface on the crystal projecting below. This is then bound to be truly parallel to the first ground surface, for the glass mounting plate is pressed into close contact with the true plane owing to the shallowness of the rabbet, and as the glass plate is a truly parallel-surfaced one it follows that the second crystal surface must be parallel to the true plane and to the first ground surface. Both the cap and the true plane are shown on the baseboard in front in Fig. 1.

This arrangement for grinding a parallel surface is shown in position on the instrument in Fig. 2, which represents the author actually grinding such a second surface parallel to one already prepared.

## CHAPTER VI

### THE SPECTROSCOPIC MONOCHROMATIC ILLUMINATOR.

THE determination of the optical constants requires monochromatic light, and for this purpose it had been customary to employ the red, yellow, and green flames obtained by volatilising salts of lithium, sodium, and thallium in the gas flame of the Bunsen lamp. Two objections apply to this method, first that it is inadvisable to confine the observations merely to three wave-lengths, the shortest of which is only in the bright green, and leaves the blue end of the spectrum quite unexplored; and second that the vapour of thallium salts is highly poisonous, and its constant use dangerous.

For these reasons, among others, a spectroscopic method was devised of obtaining light of any wave-length whatsoever, so pure as to be composed of as small a fraction of the spectrum as, for instance, would just include the two sodium D-lines, about the three-hundredth part of the visible spectrum corresponding to the normal opening of the exit slit as it is employed by the author. It enables the whole field of any optical instrument, the aperture of which does not exceed two inches, to be illuminated evenly and brilliantly with monochromatic light of this degree of purity. It is particularly suitable for illuminating the spectrometers, polariscopes, stauroscopes, microscopes, optic-axial-angle goniometers, and the other instruments employed by the crystallographer, but its applications are in addition quite universal.

A detailed description of the instrument was given to the Royal Society in February 1894.<sup>1</sup> The instrument enables the exact wave-length to be determined for which any particular phenomenon is exhibited, such, for instance, as the crossing of the optic axial planes in substances like gypsum which exhibit the phenomenon of crossed-axial-plane dispersion, of which the author's investigations have revealed six new cases in which the instrument has proved invaluable. It is shown in Fig. 3 with its principal accessories; also in

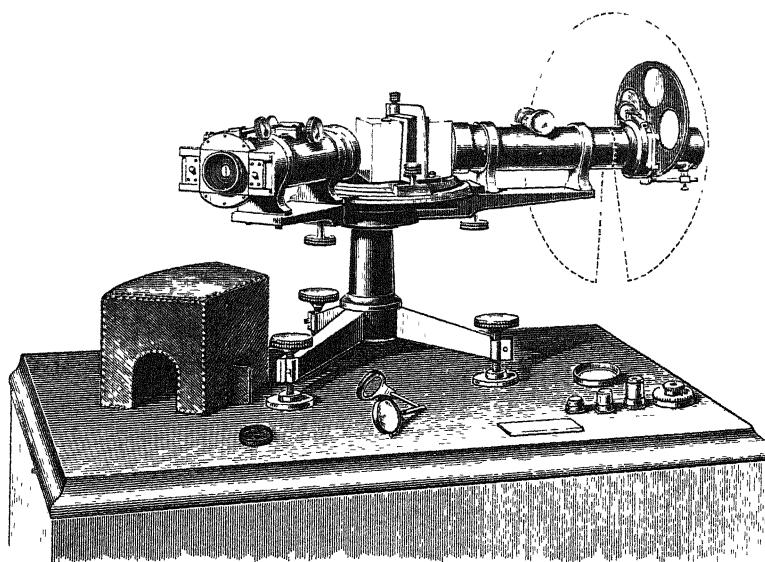


FIG. 3.—THE SPECTROSCOPIC MONOCHROMATIC ILLUMINATOR

Fig. 4 as used with the larger Fuess optic-axial-angle goniometer and illuminated with a lime-light lantern; and in Fig. 5 to illuminate the Fuess No. 1a spectrometer-goniometer as in the determination of refractive indices, the electric current being used as source of light.

The instrument is essentially a very compact spectro-

<sup>1</sup> *Phil. Trans.*, 1895, A, 185, 913.

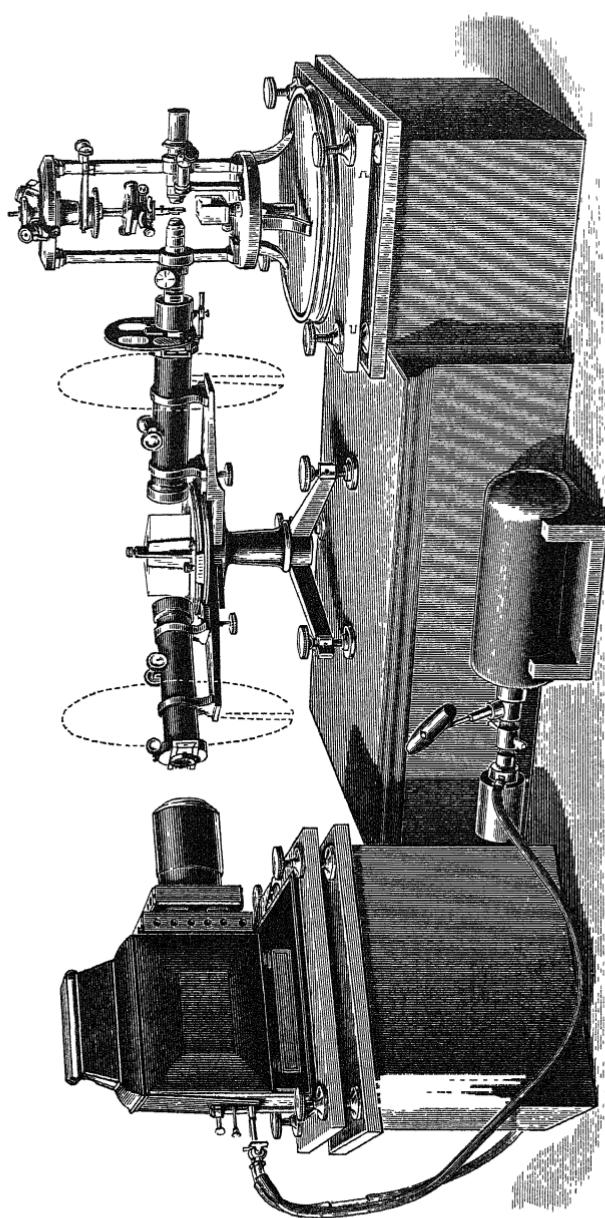


FIG. 4.—DETERMINING OPTIC AXIAL ANGLES WITH THE AID OF THE MONOCHROMATIC ILLUMINATOR.

scope, constructed with wide aperture and relatively short focus objectives and correspondingly stout optical tubes, in order to transmit as much light as possible. It was constructed by Messrs. Troughton and Simms, and the large objectives were specially designed by Mr. James Simms to give excellence of definition while passing the maximum of light, with splendid results as regards brilliance of illumination of the optical instrument which it is intended to furnish with monochromatic light, even as far into the violet as near H of the spectrum, and well beyond the hydrogen line near G.

The two optical tubes are identically constructed, consisting of wide collimators nine and a half inches long, carrying the achromatic combination objective (the two lenses of which are separated by a cooling air cell) of two inches aperture and nine inches focal length at the outer end, and an adjustable slit at the focus near the other end. Either may thus be used as collimator or as telescope, and their relative positions about the circle may be arranged quite independently as desired, counterpoises being provided to render rotation smooth. Any one of three interchangeable eyepieces magnifying respectively two, four, and six diameters, may be attached in front of either slit for the purpose of converting that tube into a telescope for observation or calibration purposes. Indeed, the instrument is then an excellent spectroscope.

The light from the lantern condenser is concentrated on the entrance slit, that is, on the slit of the optical tube which is chosen to act as collimator, and it is a great advantage to command an electric lantern which has an adjusting table for the self-feeding Brockie-Pell or Oliver projection lamp, including adjustments in all three rectangular directions of space. This enables the rays to be accurately centred, and to be made to travel symmetrically about the axis of the collimator. In Fig. 5 is also shown an arrangement of pulleys and

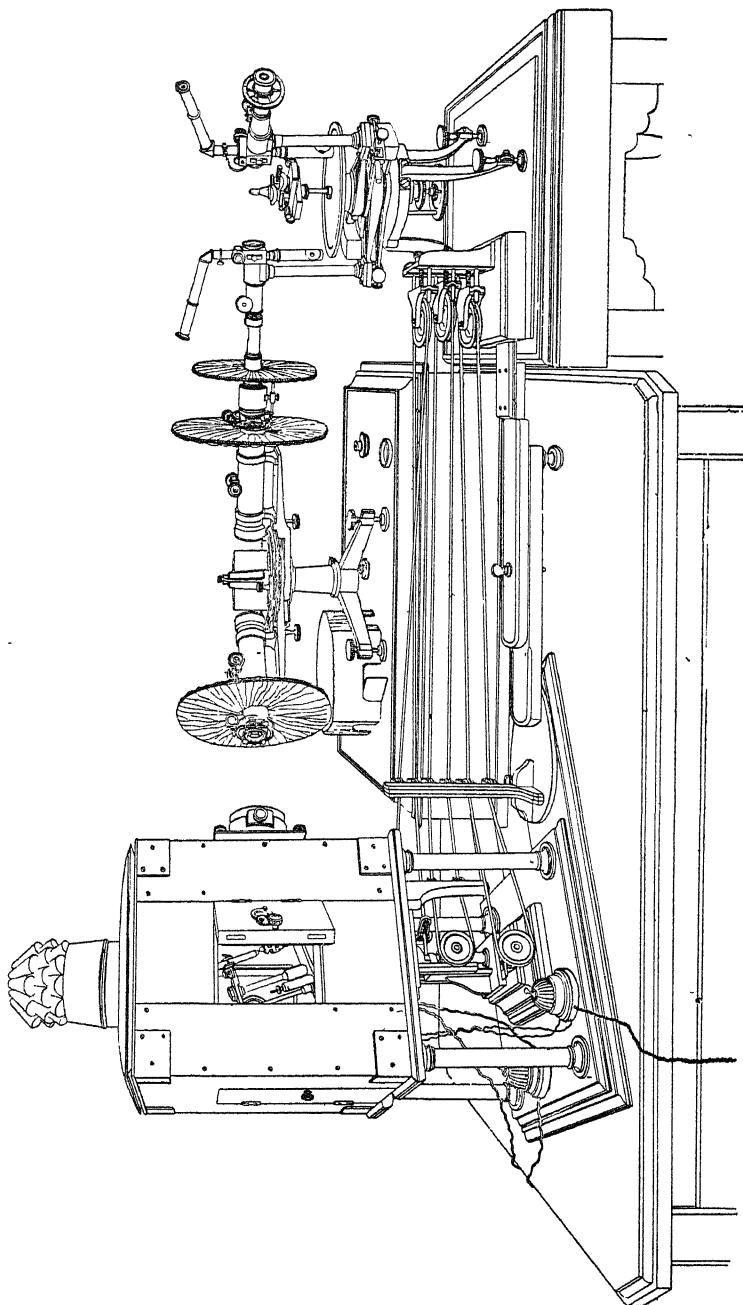


FIG. 5.—DETERMINING REFRACTIVE INDICES WITH THE AID OF THE MONOCHROMATIC ILLUMINATOR.

bands, gearing with the three adjusting wheels of the lamp table, which enables the observer to effect the adjustment of the light without leaving the observing instrument, and thus actually to observe the illumination, for instance of the images of the refractometer slit or the interference figures in the polarising goniometer, during the adjustment, and thus to see when the maximum light is obtained. The Broekie-Pell or Oliver lamp so nearly maintains a constant position of the arc that only slight adjustment is required, but this makes a great difference to the brightness of the illumination.

The dispersion apparatus consists of a single exceptionally large  $60^\circ$ -prism, of heavy yet absolutely colourless flint glass of remarkably large dispersion, the dimensions of the two refracting faces being  $4\frac{1}{2}$  by  $2\frac{1}{2}$  inches, in order that all the light which leaves the collimator objective may be taken up and the maximum quantity transmitted. Even with the lowest power eyepiece magnifying only two diameters the sodium D-lines are clearly separated, and with the second eyepiece, the one generally used, they are an apparent millimetre apart. With a little sacrifice of freedom from colour it may be replaced by a Hilger constant deviation prism, which also permits most of the spectrum to be traversed past the exit slit.

The prism is mounted on a divided circle-plate, reading directly to half-degrees and with vernier to single minutes. The fine adjustment is just sufficiently extensive ( $7^\circ$ ) to enable the whole spectrum to be traversed past the exit slit without unclamping, thus enabling the setting to be made for the issue of light of any particular wave-length with great precision, entirely by the fine adjustment screw, the head of which can be furnished with a Hilger drum calibrated directly in wave-lengths if desired. As the whole spectrum occupies about  $7^\circ$ , and single minutes can be readily adjusted, this means that the four-

hundredth part of the spectrum can be set; as, however, the width of the exit slit is somewhat greater than one minute of arc, the three-hundredth part really represents more fairly the spectrum unit which can be delivered.

The rays emerging from the exit slit of the second optical tube are allowed to impinge directly on a ground glass plate, a circular disc mounted in a cap which is capable of sliding within a short tube of similar diameter to the optical tube, and which is adjustable along a short horizontal arm of square section, carried by a ring which screws on to the optical tube instead of an eyepiece. This enables the ground glass diffuser to be arranged at any short convenient distance from the slit, and also provides a shading tube within which the objective end of the observing instrument can usually be pushed till adequately near to the ground glass screen for maximum illumination. The correct position is soon found by experience, for which a sufficiently but not excessively diffused monochromatic light-patch is produced on the ground glass to afford the best illumination of the observing instrument. Two such diffusing screens are provided, interchangeable as desired, one finely and the other very finely ground, the former being of the correct texture to fill the whole field of the polarising goniometer, when observing the rings and brushes of the interference figure, and the latter being more suitable for refractive index work, when the light is more advantageously concentrated in the middle of the field in the image or pair of images of the goniometer-spectrometer Websky slit. This slit—the usual goniometer signal, broad at the two ends to pass plenty of light and narrowed till barely wider than a spider line at the centre in order that it may be placed with great accuracy to the vertical cross-wire—is used for determining the refraction by means of the  $60^\circ$ -prisms prepared with the aid of the cutting and grinding goniometer described in the last chapter, rather than an ordinary spectrometer.

straight slit, for obvious reasons. Hence, whenever refractive indices are to be determined, the clearer ground glass diffuser is used, but when an optic axial angle is to be measured, the coarser diffuser is placed in the short diffusing tube instead.

A very useful adjunct for use in observing interference figures in the less brilliantly illuminating parts of the spectrum, notably the violet and, less markedly, the blue and greenish blue and the extreme red—when a little white light may stray into the field by reflection from the various glass surfaces or by diffusion, even when the objectives and prism are boxed in with a velvet-covered cardboard shade—is a double window of coloured glasses, which may be introduced when desired between the exit slit and diffusing tube. This device to get rid of such disconcerting stray white light, which is particularly obnoxious when studying the interference figures in violet light of substances showing crossed-axial plane dispersion, the author owes to Sir William Abney, to whom also he is indebted with regard to the principle of the instrument. Ruby red glass readily removes this white light without interfering with the red spectrum light, Chance's signal-green glass likewise acts efficiently to remove all other rays when one is working with the greenish blue, and two glasses, one of signal-green and the other of cobalt-blue, together remove all trace of white light when observations are being made with the spectrum violet.

Hence, a couple of large circular discs were constructed, and each pierced with four circular windows, like a quatrefoil. One window of each was left blank (open) for use when the coloured glasses are not required, as in refractive index work; one of each disc was filled with ruby red glass, another with signal-green, and the fourth with cobalt-blue glass. The two discs are so mounted on a common axis that they are capable of

separate rotation, the edges being milled; so that the two open windows can be left opposite the slit when no glass is desired to be interposed, and either any one single glass or a pair, the combination of signal-green and cobalt blue for instance, may be brought between the slit and the diffusing screen at will.

The cutting and grinding goniometer, described in the last chapter, enables the  $60^\circ$ -prisms of doubly refracting crystals always to be cut so as to furnish both indices of refraction if uniaxial, or two of the three indices if biaxial, directly. Hence, unless the crystal belongs to the cubic system, and has, therefore, only one index of refraction, two images (with good crystals, brilliant magnificently coloured objects in the monochromatic light supplied by the illuminator) of the Websky signal slit will always be seen in the field of the spectrometer, one of which, that having vibrations parallel to the refracting edge of the prism, will extinguish when the Nicol in front of the eye-piece is at  $0^\circ$ . The other, slightly stronger image, the direction of vibration of which is perpendicular to the prism edge, and to the minimum deviation direction of transmission, and lies in the plane bisecting the prism angle, extinguishes when the Nicol is at  $90^\circ$ .

To calibrate the circle readings in wave lengths, the middle power eye-piece magnifying four diameters is screwed into position in front of the exit slit instead of the diffuser, and the jaws of the slit are clearly focussed.

The entrance slit is then illuminated in succession with sunlight, and with sodium, lithium, and thallium flames, and also with a hydrogen Geissler tube, and the principal Fraunhofer or bright lines focussed and brought in turn midway between the jaws of the exit slit, and the circle reading for each recorded.

It is advisable also to determine the readings for the red, green, and blue lines of cadmium, and for the green

line of mercury, with the aid of Geissler tubes, as these rays are now much used in optical work.

A curve has been constructed to pass through all the recorded readings, circle readings forming one set of co-ordinates and wave-lengths the other, so that the readings for the issue of light of intermediate wave-lengths from the exit slit can be determined by interpolation. Moreover, a Hilger drum can be fitted to the fine adjusting screw of the circle, and the wave-lengths directly marked on it.

Having thus calibrated the instrument, the eyepiece is removed and the ground glass fitting placed in position before the exit slit instead. When the entrance slit is illuminated with white light from the electric arc or lime light, the former being vastly preferable as being more intense and more nearly a radiant point, monochromatic light, of the wave length indicated by the curve or drum for the particular circle reading to which the instrument happens to be set, issues from between the jaws of the exit slit, and illuminates the diffusing screen with a brilliant patch of coloured light, adequate to fill the whole field of any observing instrument set in front of it.

Throughout the author's investigations the wave-lengths employed for the determination of all the optical constants have been those of the three above-mentioned metallic lines, namely, the red lithium line, yellow sodium D-lines, and green thallium line, and also those corresponding to the three hydrogen lines, the red C, greenish-blue F, and the violet line near G.

This instrument and the one described in the previous chapter, the cutting-and-grinding goniometer, have proved so invaluable that the author most strongly recommends their use in all future crystallographic investigations. Whatever value his optical work may have is largely owing to them.

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## CHAPTER VII

### THE INTERFEROMETER.

Two further instruments which the author had to devise and which have also proved highly successful are: (1) an interference dilatometer, for measuring the thermal expansion of crystals and indeed of solid substances in general on Fizeau's principle, and (2) an interference clasmometer, for measuring their elasticity by determining the amount of bending which a plate of the crystal or other solid substance undergoes at the centre, when supported near its ends, under the influence of a weight applied at the centre. The essential optical part is common to the two instruments, and constitutes the "interferometer," which is, in fact, an apparatus for fine measurement in general by the interference method.

The optical principle involved is the interference of absolutely homogeneous monochromatic light waves, corresponding strictly to a single line of the spectrum, by reflection from two truly plane surfaces, one of glass and the other of the crystal or other object, or something moving with it, generally an aluminium or black-glass plate. These two surfaces relevant to the interference are arranged somewhat under a millimetre apart, and in approximate but purposely not quite exact parallelism, so as to produce, by the interference of the waves of light derived from the same original source and severally reflected from them, rectilinear dark interference bands on a background of the coloured strictly monochromatic light.

The change of position of these bands, moving parallel to themselves and perpendicular to their length, when the crystal or other object under measurement expands, contracts, or moves, and its surface consequently approaches or recedes from the glass surface, affords an absolutely accurate and extraordinarily sensitive measure of such small movements. For the passage of each band past a reference mark at the centre of the glass surface corresponds to a movement equal to the half wave-length of the light employed.

If a ground and polished surface can be prepared on the crystal itself, this acts in the dilatometer as one of these two reflecting surfaces relevant to the interference, but if the crystal is unpolishable, the upper polished surface of a disc of aluminium lying on the crystal is arranged to move absolutely along with it and to represent it; the second reflecting surface is furnished by the colourless glass disc, which the light has to pass perpendicularly through twice, on its way to and from the crystal surface or whatever surface acts for the latter. In the clasmometer, the polished plane surface of a black-glass disc is used anyhow, whether the crystal is polishable or not, instead of the crystal surface, being in rigid connection by a pointed connecting rod with the centre of the latter, the position of maximum bending of the crystal-plate during the experiment. For by reason of the bending the crystal surface is not itself suitable for the direct production of bands. Black glass has the advantage that while being of similar reflecting power to the colourless disc, any penetrating light, which is not required, is absorbed and thus got rid of; to complete this extinction the back surface is ground.

The colourless glass disc has obviously a second surface besides the one which approaches the crystal surface or its substitute, and light is reflected also from this surface, which if not eliminated would disturb the sharpness of

the dark interference bands by illuminating them. This colourless disc, therefore, is not a truly parallel-sided plate, but a wedge or prism of very small angle, the two absolutely truly plane surfaces being inclined at an angle of 35 minutes. This is just adequate to cause the light reflected from the second surface to be directed out of the field of view of the telescope eye-piece, an iris diaphragm enabling it to be screened off efficiently. A little prismatic dispersion is, however, introduced by the device, and this is corrected by means of a duplicate wedge, cut from the same large plate which had been preliminarily ground to the 35' angle. These disc-wedges are between 4 and 5 centimetres in diameter and nearly a centimetre thick for the sake of rigidity. Both are marked to show the direction of the wedge by two engraved marginal dots at the thicker end and a single dot at the thinner end of the wedge-direction diameter. They are adjusted so that their wedge-directions are parallel, but with the thicker end of one opposite the thinner end of the other, when the prismatic effect is corrected; to eliminate the two reflections from the countervailing duplicate, this second wedge is given a minute tilt, about three-quarters of a degree sufficing, at right angles to the direction of the wedge, when its reflections are similarly screened off by the iris diaphragm of the telescope.

If the air film between the two closely adjacent reflecting surfaces relevant to the interference were of equal thickness throughout, that is, if the truly plane surfaces were strictly parallel, alternate fields of the brilliant monochromatic light and of jet-black darkness would be observed as the distance of separation of the surfaces was varied by moving one of the surfaces normally and parallel to itself. But when the air film is made slightly wedge-shaped, by tilting one of the discs, then rectilinear interference bands (lines of extinction) are produced, the width of which diminishes as the tilt

increases and which rotate if the position of the edge of the air-wedge (that is, of the direction of tilting) is altered.

The thickness of the air film should not matter theoretically if the light were absolutely monochromatic, that is, if the spectrum line corresponding to it were single and absolutely unresolvable into a double line or a triplet by extreme dispersion. Practically it does matter. With light corresponding to the red line of cadmium vapour, the only suitable line that has yet resisted resolution, the bands can be seen when the surfaces are as much as a decimetre apart. With light of the wave-length of the green mercury line, the interference bands are still visible for a separation of the surfaces of between one and two centimetres. But with red C hydrogen light, the surfaces must not be further apart than about three millimetres, and between half a millimetre and a millimetre is the best distance of separation for brilliant bands, in either this or greenish-blue F-hydrogen light.

The object in producing rectilinear bands, rather than the usual circular interference rings, as used by Michelson and by Fabry and Perot, or broad fields of light and darkness, is to render the extinction lines suitable for micrometric measurement, and to obtain a field containing several such dark bands as narrow parallel lines separated by broad brilliantly illuminated interspaces, so that the distance between the blackest central part of two adjacent bands can be determined in micrometer drum readings, by measuring it between successive pairs of bands, the average of which will give a very accurate quantity, usually not less than 100 drum divisions, for the true "width" of a band.

The light employed for all ordinary purposes is that of the red hydrogen ray  $H\alpha$ , the C of the solar spectrum. The wave-length of this light is 0.0006562 millimetre, and the half-wave-length consequently 0.0003281 mm., that is,  $\frac{1}{3048}$  of a millimetre, or  $\frac{1}{77419}$  of an inch. Assuming

the band-width to be 100 micrometer divisions, the one-hundredth part of this is the unit of measurement of the instrument, namely in round numbers, the three-hundred-thousandth of a millimetre or the eight-millionth part of an inch. This fineness of measurement is truly wonderful, and it is rendered all the more so when the absolute accuracy is remembered. For a minute error in dividing a scale may be possible even to the best dividing engine, but the scale of interference bands cannot deceive, for they are the direct product of a natural phenomenon the precision of which lies almost beyond our conception. The only possibility of error comes in with the determination of the width of a band, and as a drum can be accurately divided into a hundred parts with ease, the only possible error here is one of judgment in the placing of the band symmetrically between the two parallel vertical spider-lines, and that cannot possibly exceed two drum divisions after reasonable practice.

The "interferometer" includes the interference apparatus (the two colourless glass wedge-discs and the crystal or other object or its representative), the apparatus for producing the monochromatic light, directing it normally upon the interference apparatus, and for receiving the interfering rays returning along the same identical path, and that for observing the bands which they produce. With the exception of the mode of mounting the discs, and the dispersion apparatus (a glass prism or prisms) which selects the rays of light of the desired wave-length and deflects out of the field of the observing telescope eyepiece all other rays, the interferometer is an instrument of common construction whatever the object of the measurements may be. It is represented, without the above variable parts, in Fig. 6.

It consists of an auto-collimating telescope on a strong pedestal, adjustable for height by rack and pinion and terminating below in a tripod base adjustable by levelling

screws ; the pedestal is mounted on the tripod in such a manner as to be further adjustable by two horizontal lateral and front-and-back movements at right angles to each other, constructed of great strength and manipulated by two hand-wheels as shown in Fig. 6. The source of light

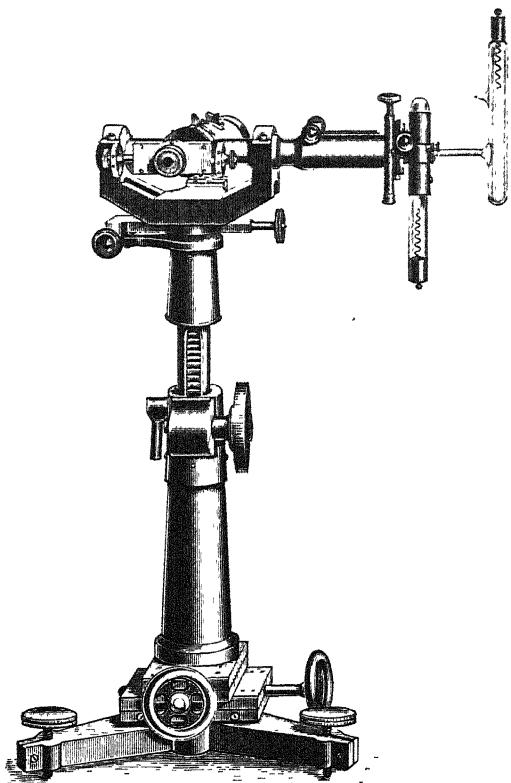


FIG. 6.—THE INTERFEROMETER.

is the capillary horizontal connecting tube of a H-shaped hydrogen Geissler vacuum tube, provided with spiral aluminium terminals to avoid occlusion of the hydrogen and alteration of the degree of vacuum favourable for the production of the red-glow, when the intermittent secondary current from the Ruhmkorff coil is passed

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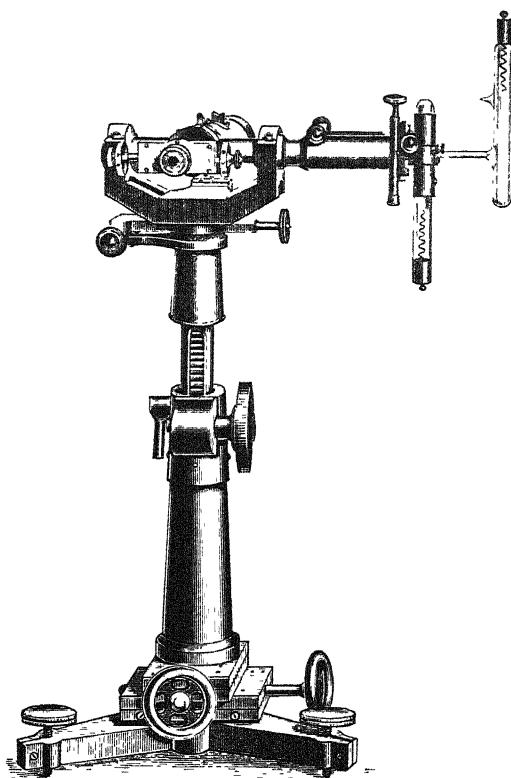


FIG. 6.—THE INTERFEROMETER.

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through the tube. It is necessary, when working with long distances of separation of the reflecting surfaces of the interference apparatus, to replace the red C-hydrogen light by the rays of the red line of cadmium, wave-length 0.0006438. For this line has proved to be the only one which has resisted all efforts to resolve it into components, thus indicating its perfect homogeneity and consequent freedom from secondary interference ; whereas under great resolving power, such as that of the Michelson echelon spectroscope the red hydrogen line is seen to be really double. The secondary interference which results from this doubling of the hydrogen line, however, only becomes apparent at a distance of separation of the surfaces of about 3 millimetres ; so that for all ordinary purposes, when the surfaces are used in close proximity to each other, somewhat less than a millimetre of air-film separating them, it is equally as satisfactory as the cadmium ray, and much more convenient, for the cadmium tube requires to be heated to a temperature of over 200° before the cadmium spectrum is produced, whereas the hydrogen Geissler tube works at the ordinary temperature.

The interference bands may also be produced in the greenish-blue F-hydrogen light ; they are then closer together on account of the shorter wave-length, 0.0004861. The colour of this light is particularly agreeable to the eyes, and provided the bands are widened by a minute adjustment of the colourless glass disc they are equally suitable for measurement purposes. Sodium light is altogether unsuitable, however, although it was used by Fizeau. For the wave-lengths of the two D-lines being so far apart as  $D_1 = 0.0005896$  and  $D_2 = 0.0005890$ , secondary interference soon begins to destroy the sharpness of the bands when either of the surfaces is moved ; the bands, in fact, disappear at regular intervals.

Occasionally, as during the determination of the thermal expansion of the platinum-iridium screws of the inter-

ference tripod of the dilatometer, it is convenient to use the rays corresponding to the green mercury line, wavelength 0.0005461, as the interference bands given by them are visible at as much as a couple of centimetres' distance of path, quite enough to cover the length of the screws. In this case a special hydrogen tube having a globule of mercury also enclosed is employed. For use in the preliminary adjustment of the surfaces of the interference apparatus, when the images reflected from them of a rectangular stop in front of the source of light have to be reviewed, a source of bright white light is required. This may conveniently be a goniometer lamp—a tantalum or Nernst electric lamp with clouded glass globe or diffusing screen; it should be enclosed in a metallic cylindrical shade which only allows the light to pass out from an aperture about an inch and a quarter in diameter, which is placed opposite the auto-collimating side tube, the Geissler tube fitting being removed.

As regards this latter, the vacuum tube is mounted in an adjustable manner, both for centring and distance from the collimator objective, in a fitting with spring holder lined with felt, carried at the end of the collimating side tube, shown to the right in Fig. 6 and above in the plan of the optical tubes which is given in Fig. 7, which also shows the general plan of the whole interferometer. The direct support for the Geissler tube *u* (Fig. 7) fitting is a short tube *x* sliding over an inner one, *w*, by rack and pinion; the tube *w* slips over the collimator to a convenient position, in which by use of the rack and pinion the brilliantly illuminated end of the horizontal capillary of the Geissler tube, or any section along the capillary where the maximum red light is found, can be focussed by means of the collimating lens *d* on to a small totally-reflecting prism *h*. This latter is adjusted at the rectangular junction of the collimating tube *e* and the telescope *a*, where it covers exactly one-half of the

circular aperture of the diaphragm *g*, which is here inserted at the focal plane of the telescope objective *b*. The aperture may be further narrowed down by means of an iris diaphragm *f*, the function of which is to exclude all undesirable reflections.

The actual origin of the light waves which are to interfere is a small rectangular stop *k*, which has already

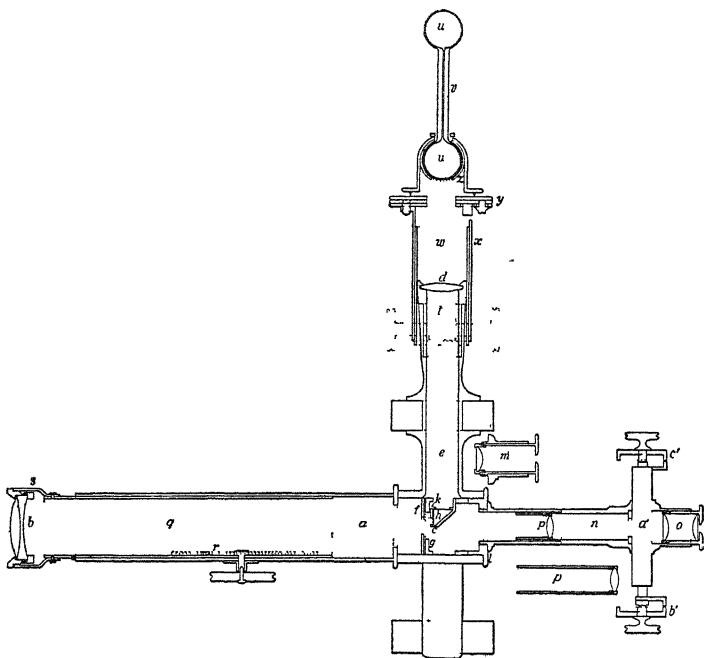


FIG. 7.—PLAN OF INTERFEROMETER AUTO-COLLIMATING TELESCOPE.

been alluded to as furnishing by its images reflected from the surfaces of the interference apparatus the means of adjusting those surfaces; a series of such stops are provided, fitted with little handles at their upper end to enable them to be inserted conveniently into a niche cut in the top of the telescope tube to receive them. The stop generally used is one of 3 millimetres by 2 in size of aperture, one of the longer (3 mm.) edges of the aper-

ture of which is quite close to that edge of both stop and prism which abuts on the open half of the diaphragm aperture *c*; the edge of the prism-case actually forms the diametral line which marks off the open half on the left from the closed half (closed by the prism and its case) of the aperture on the right. Hence the rectangular aperture of this stop is situated within a millimetre of the telescope axis. This enables the condition for identical paths of the light incident on and reflected from the interference surfaces to be practically attained, for the two images of the rectangular stop as reflected from the interference surfaces are actually focussed by the eyepiece within two millimetres of the actual stop itself, and are then adjusted to the best position for interference to occur, which is when they almost but not quite completely overlap.

After reflection by the little prism the rays pass through the rectangular stop to the objective *b*, at the focus of which the stop is situated, so that after filling it with light they pass out to the dispersion apparatus as parallel rays, from whence they are deflected perpendicularly on to the interference apparatus. After reflection there they return to the objective by the same path, re-enter it, and pass on to its focal plane. But here, instead of striking the stop again, they are arranged to pass, as above stated, slightly to one side of it, through the open half of the diaphragm *c* to the eyepiece.

When observing the images of the stop in the preliminary adjustment of the surfaces, and adjusting them to the correct positions for interference, a simple eyepiece is employed, shown by itself at *m* in Fig. 7; but when observing the interference bands a compound eyepiece of special construction, shown in position at *n*, is used. The simple eyepiece focusses clearly the semi-circular open aperture, the edge of the prism-case appearing as a sharp vertically diametral dividing line between the

open and closed halves ; and the images of the stop from the various surfaces are to be brought into this open half, where, when all is properly arranged, they appear also sharply defined, white light being used. The special eyepiece, however, converts the telescope into a low-power microscope, which focusses clearly that surface of the colourless glass wedge-disc which is nearest to the crystal surface or other surface representing it (black glass or aluminium), and is one of the two surfaces concerned in producing the interference. The centre of this surface bears a miniature silvered reference ring, which also serves as an admirable object to enable the surface to be focussed by. It is found by experience that when this ring is sharply focussed, the interference bands are also at their maximum sharpness of definition. Moreover, the semicircular character of the aperture is now no longer apparent, as it serves but as a common focal diaphragm for the shutting off of the undesirable reflections from the glass surfaces non-relevant to the interference ; instead one sees a full circular field, the image in fact of the surface of the colourless glass wedge-disc just referred to, concerned in the interference. The other and smaller of the two reflecting surfaces relevant to the interference, and which is obviously the crystal, black glass, or aluminium surface, appears as a brilliant red (or whatever colour of light is being used) disc almost filling the whole field of the eyepiece, and crossed by the jet-black interference bands, arranged, when adjusted, vertically. Fig. 8 gives a fairly faithful representation of the appearance of the field. The "comb" or rough scale of the micrometer, seen below the bands in Fig. 8, is adjustable, so as to be quite clear of the circular field of bands.

This special eyepiece consists of an ordinary micrometer eyepiece  $o$  and an additional lens  $p$ , whose position can be varied in the somewhat long body-tube  $n$ , to suit various distances of the interference apparatus from the telescope,

now a microscope, which has to focus the interference apparatus. As this distance is the same for the particular experimental work in hand it is found more convenient not to move  $p$  by rack and pinion, but to mount it in one of several interchangeable inner tubes of varying lengths, half a dozen being supplied with the apparatus, ranging from  $p$  to  $p'$ . The micrometer  $a'$  has a parallel vertical pair of spider-lines, one of which is movable alone so as to be

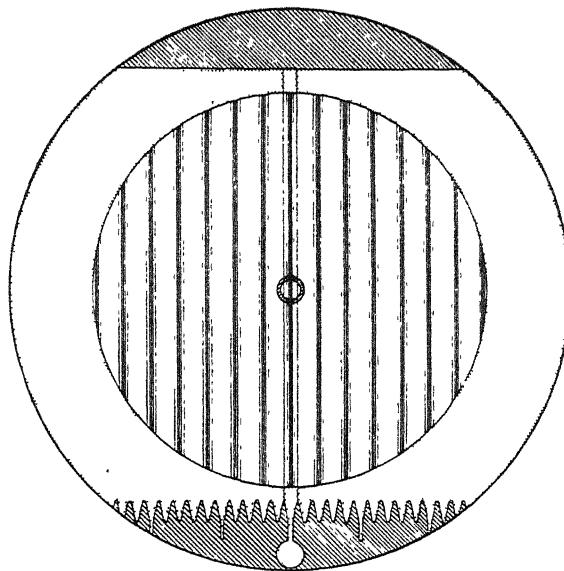


FIG. 8.—THE FIELD OF INTERFERENCE BANDS

capable of being set to any distance of separation from the other, the left-hand drum  $b'$  effecting this movement, which may be measured in drum-readings if desired; the right-hand drum  $c'$  moves both lines simultaneously, and one revolution corresponds to a very convenient width of interference band. Hence, when the separation of the spider-lines is arranged so that a band may be adjusted so as to lie altogether and symmetrically between them, still showing a little line of light on each side as shown in

Fig. 8, the width of a band may be determined by traversing the two spider-lines together from this position until the next band is similarly adjusted, and will amount to not less than a complete revolution—one hundred drum divisions.

The position of the telescope for altitude is capable of accurate adjustment by a vertical screw and determination by means of a scale, and of being re-set at any time to the adjustment for any spectrum line, and for the production of the interference bands in that colour.

A second pedestal like that of the telescope supports the dispersing and interference apparatus, and the general plan will be clear from Fig. 9. A wide tube *rp* is suspended vertically by a horizontal arm *q*, adjustable for azimuth by rotation about the pedestal top; the upper and lower parts are of brass, but the intermediate part *p* is constructed of the best Berlin porcelain, in order to avoid conduction of heat from the lower part, which is to be heated in a hot-air bath *yz* when the instrument is employed as dilatometer. The attachment of the porcelain is made by means of springs *u*, flanges *vs*, and a screwed supporting ring *t*, the porcelain tube itself having a flange *s* at each end for convenience of this attachment, so as to avoid any strain due to difference of expansion. At the top the metal end *r* of the tube carries a pair of dispersing prisms, adjusted to give together a total minimum deviation of just  $90^\circ$  for the middle part of the spectrum. The carrying frame of these prisms slides in dovetailed grooves in a fitting *w*, which is rotatable within the tube *r* in order to give a separate azimuth adjustment, and the rack and pinion on the pedestal affords the vertical adjustment. Each prism is set independently to minimum deviation for sodium light, and the position is indicated on a silver divided arc (seen in Fig. 11), so that if the reading is noted it can always be regained if by chance it gets deranged. The lower end of the tube.

bears a screw thread  $f$ , and down to this point the whole of the apparatus is common to dilatometer and elasnometer.

For the purpose of preliminary adjustment the two refracting prisms are replaced by a single totally reflect-

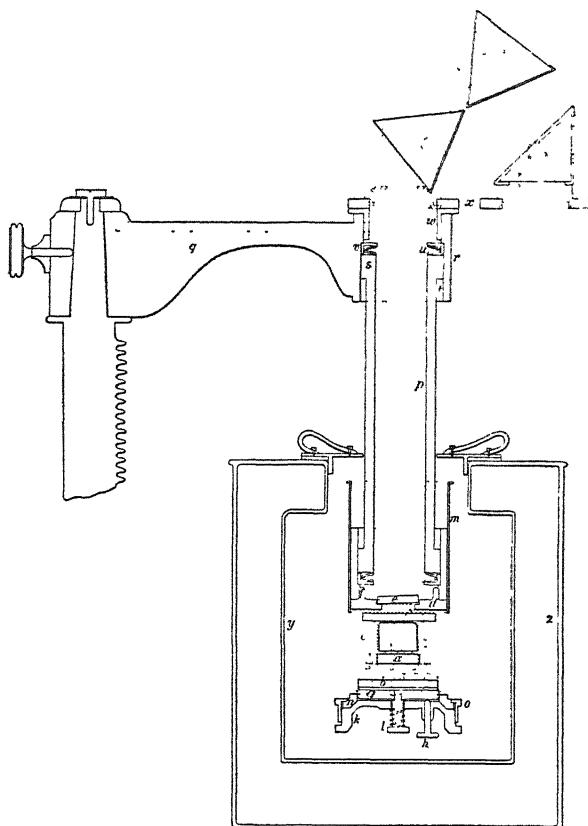


FIG. 9.—SECTIONAL ELEVATION OF DISPERSING TRAIN AND INTERFERENCE APPARATUS.

ing prism  $x$ , adjustable about a horizontal axis, and similarly mounted to fit in the dovetailed grooves of the rotatable annulus about the tube top, so as to be also adjustable for azimuth.

For the purposes of the elasmometer there gears with the screw thread  $f$ , just referred to as being carried at the lower end of the tube, a simple cap  $d$  with central aperture of one inch diameter, which latter is rabbetted to take the countervailing duplicate colourless glass wedge-disc  $e$  of  $35'$  angle (a diameter of one inch sufficing in the case of this wedge-disc); the rabbet has two raised points  $120^\circ$  apart to tilt the disc just adequately to throw both of its reflections out of the field of the telescope. This can be adjusted to a nicety, as the raised points are the ends of two little screws passing through the rabbet to an extent which can be regulated from below. The suspended tube is arranged so that this cap carried at its lower termination is brought closely over the interference apparatus carried on the elasmometer itself, which will be described in Chapter IX.

The author has described the interferometer at some length, not only because it is common to the dilatometer and the elasmometer, but also because it has now proved itself to be an important instrument of universal utility, and to afford the highest accuracy and refinement yet attained in the fine measurement of all kinds of minute movements or short distances, of which the measurement of thermal expansion and of elastic bending are only two examples.

A very fine instrument has lately been installed at the Standards Department of the Board of Trade, for the comparison of standards of length with copies, both line and end-measure bars, in wave-lengths of red cadmium or hydrogen light. The basis of the instrument is the interferometer as here described, and for details the memoir in the *Philosophical Transactions of the Royal Society* (1909) should be consulted, but Fig. 10, taken from that memoir by the kind permission of the Council of the Royal Society, shows the arrangement of the interferometer. A Hilger constant deviation prism is in position

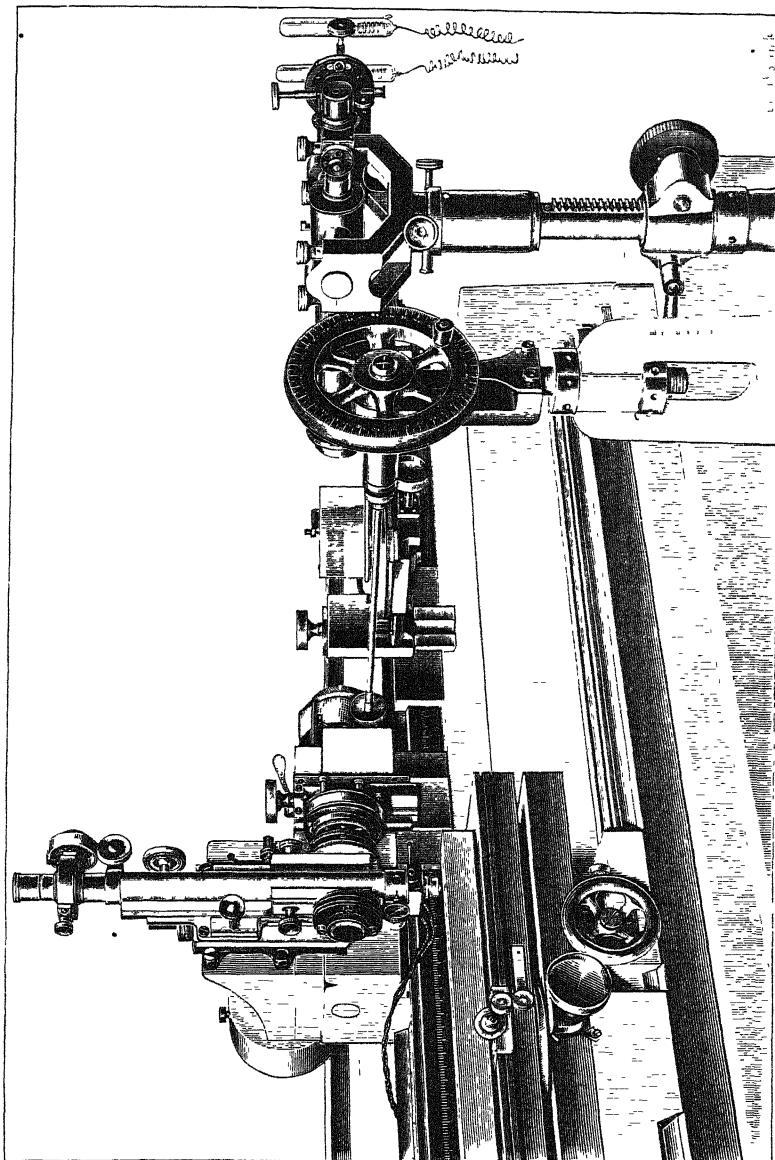


Fig. 10.—INTERFEROMETER OF STANDARD COMPARATOR.

as the dispersing apparatus, horizontally arranged. The colourless glass wedge-disc and its counteracting duplicate (in this instrument exactly of the same size) are mounted vertically in an adjustable manner in a fitting also adjustable, but which is finally clamped rigidly to the solid V-and-plane bed on which the two microscopes slide which focus the defining marks on the standard bar. The right-hand microscope carries the black-glass interference disc, which thus moves with the microscope in close proximity to the colourless glass wedge-disc. The amount of the movement is absolutely recorded by the movement of the interference bands, being equal to half the wave-length of the light employed for every band which passes the reference spot.

In order to compare two bars, (1) the standard bar is arranged on an elaborate adjusting table sliding on a second lower V-and-plane bed, so that the two defining lines near the ends of the bar are focussed by the two microscopes and adjusted to the spider-lines; (2) the standard is replaced by the copy to be compared, and the left defining line adjusted under its microscope; then, if the right defining mark is not also thereby adjusted under the right microscope carrying the black-glass interference disc; (3) that microscope is traversed until it is so adjusted, by rotation of the large fine-adjustment wheel (in front in Fig. 10), which effects the excessively slow and steady motion of the slider which carries the microscope; (4) during this latter process the interference bands are counted as they pass the reference spot.

The fineness of the sliding movement of the microscope, its absolute steadiness, and the perfect control over it, are the essential features of the apparatus which have rendered it so successful as regards its specific object, and have constituted it the most accurate measuring instrument in existence at the present time.

## CHAPTER VIII

### THE DILATOMETER.

For the purposes of the dilatometer, the general aspect of which is shown in Fig. 11, an interference chamber *c* (Fig. 9) gears to the screw thread *f*, instead of the cap at the bottom of the suspended tube of the interferometer. It takes the form of a prolongation of that tube in gun-metal, but the greater part of the wall is cut away to form three windows, leaving three narrow supporting pillars connecting the roof *d*, which resembles the cap just referred to, with the base *g* of the chamber, which is adjustable for level by three milled-headed screws *h* worked from below. The rabbeted aperture of the roof plate takes the countervailing wedge-disc *e*, which also serves to render the central part of the roof non-conducting; it is tilted slightly by two screw points as when used in the cap for the purposes of the elasmometer.

The Fizeau tripod *a* is supported within the chamber on a glass plate *b*, which rests on a disc of asbestos laid directly on the adjustable floor *g*. In the author's instrument the tripod is constructed of solid platinum-iridium (10 per cent. of iridium), and its appearance is shown at *a*, *b*, and *c* in Fig. 12.

\* An object for determination of thermal expansion by the ordinary Fizeau method is shown at *a* in Fig. 12, resting on the outer set of three raised points. The 35' wedge-disc is also shown resting on the tripod screws. For the three legs of the tripod are screws with a very fine

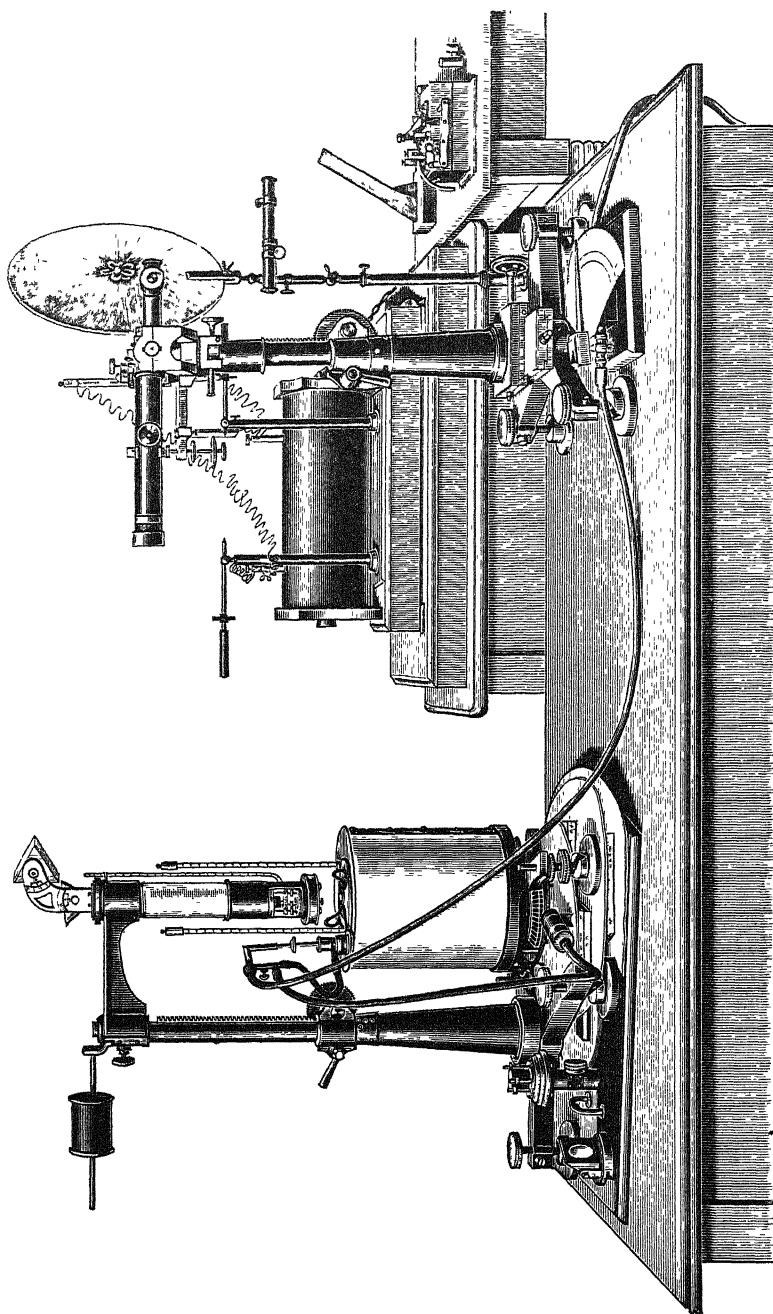


FIG. 11.—THE DILATOMETER.

pitch and 3·5 centimetres long, passing through three correspondingly tapped short arms of the table 7 millimetres thick, also of solid platinum-iridium. Each screw carries a milled head near the end which is normally the lower one, and both ends are more or less bluntly pointed; little tightening screws pass sideways through the arms which are slit for tightening purposes, in order to fix the screws in the adjusted positions. The surface of the table normally placed uppermost, as at *a* and *b* in Fig. 12, bears three concentric sets of three raised points, each set of a different height increasing towards the circumference of the table, so that crystals or other objects

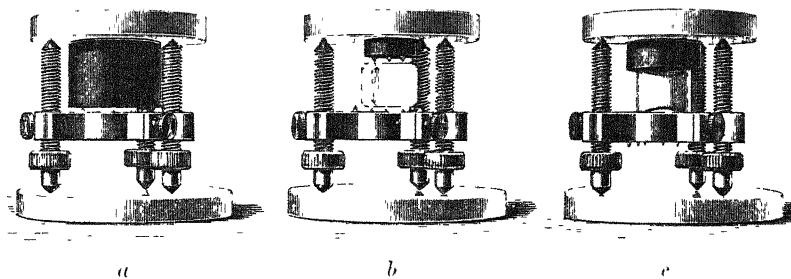


FIG. 12.—THE INTERFERENCE APPARATUS.

for thermal investigation of different sizes can be accommodated by the three-point method of support, the only rigid method which avoids air-films or other disturbing circumstances. The other surface is a true plane and highly polished, and is used uppermost as at *c* in certain cases when found desirable, such as in the investigation of a soft substance which might be penetrated by the points, and particularly when the expansion of the screws themselves is to be determined, when the table itself is made to act as one of the reflecting surfaces productive of the interference. For the essence of the method is that the actual quantity determined is the difference of expansion of the platinum-iridium screws (this metal being not only

unalterable but having a relatively very low expansion) and of the object resting on the platinum-iridium table, so that the preliminary determination of the expansion of the platinum-iridium alloy is of fundamental importance.

At *b* the tripod is shown with a crystal, the thermal expansion of which is to be determined, *in situ* together with the 35' wedge-disc, and a small but relatively thick disc of aluminium which rests by three points on the crystal when the surface of the latter is not adequately polishable. Black glass may be used instead of aluminium, but the latter has advantages which will presently be discussed, although it requires to be kept in a desiccator when not in use on account of possible tarnishing in moist air. The case shown at *c* in Fig. 12 is a special one investigated by the author, that of the expansion of Bayeux porcelain, a section of a tube of the porcelain having been employed, and a cover-disc of aluminium. The latter is here invaluable, the porcelain being unpolishable.

Immediately below the suspended tube is a double cylindrical air-bath *yz* (Fig. 9) of copper, covered outside with asbestos. The tube can be lowered into the inner bath *y* by means of the rack and pinion of the pedestal, and is finally arrested when the interference chamber occupies a position slightly below the centre, so that a small part of the porcelain portion of the tube is also immersed. A mercury Muencke thermostat is placed in the outer bath, as shown in Fig. 11, which, together with a Stott governor introduced between the gas supply and the apparatus, and with the aid also of a finely graduated gas tap shown on the table to the right in Fig. 11, enables a constant temperature to be maintained at any height between the ordinary temperature and 120° C. In the inner bath are two thermometers, but the actual temperature of the platinum-iridium tripod and its contents is measured directly by a third thermometer, specially constructed by

Messrs. Negretti and Zambra, which is bent at right angles just above the bulb, in order that the latter may rest on the platinum-iridium table almost touching the crystal or other object the expansion of which is being determined. It is arranged that this thermometer shall be read by a telescope a couple of yards distant, seen to the right of the interferometer in Fig. 11. When the interference chamber has been lowered into position the top of the bath is closed with a lid, which is fitted on in two halves and is lined underneath with asbestos. The adjustment of the interference apparatus is carried out while the bath is removed from its supporting ring, below which is the Bunsen gas burner, with several concentric rings of jets.

If the crystal or other solid substance the thermal expansion of which is to be determined is polishable, and the polished surfaces are capable of withstanding a temperature of  $120^{\circ}$  C., the limit to which so far the method has been carried, it is only necessary to prepare a block of it about a centimetre thick, by cutting or grinding and subsequently polishing a pair of parallel surfaces a centimetre apart if the crystal is large enough to furnish such a block. The ideal size is 12 millimetres thick and from that to 15 millimetres (or even up to 2.5 centimetres in case of material procurable in quantity) in diameter, supposing the crystal or other object to be more or less cylindrical in shape, the axis of the cylinder being of course upright and the two parallel polished surfaces forming its ends. This is the case shown at *a* in Fig. 12. The shape of the crystal, however, matters very little, provided the two essential parallel surfaces are a centimetre apart and that there is sufficient width to ensure stability on the three points or the polished table surface. If the latter is used the crystal must be pushed along it in a sliding manner, in order to remove any air-film.

The best surface as regards polish and planeness is

chosen for the upper reflecting surface. By planeness, in the case of the preparation of surfaces for use in interference band production, the very highest perfection is to be understood. A surface which is plane to all ordinary optical tests, such as those of reflection, often gives most irregular bands, due to want of the highest order of planeness.

If the crystal or other object of the investigation is unpolishable, or inadequately so, or if its polished surfaces will not withstand a temperature of  $120^{\circ}$  C., a small but relatively thick disc of aluminium, having three points raised from one of its surfaces, is laid over it so as to rest on it by the three points, as shown at *b* in Fig. 12. The upper surface of the disc of aluminium, which is truly planely polished, then serves as the reflecting surface instead of the upper crystal or object surface.

As aluminium expands about 2·6 times as much as platinum-iridium, it is easy to choose a disc, out of a series prepared for the purpose, which will roughly compensate for the expansion of the lengths of the platinum-iridium screws which project above the table of the same alloy on which the crystal or other substance under investigation rests. By so doing, approximately the whole expansion of the substance is recorded by the movement of the interference bands, affording at once an idea of its relative expansibility, or in the cases of contraction occasionally met with, indicating the fact immediately.

The author's values for the expansion of platinum-iridium and of aluminium, which are used in the calculations, and agree well with those obtained by Benoit and by Fizeau, are as under:—

Mean coefficient of expansion,  $\alpha + bt$ , between  $0^{\circ}$  and  $t^{\circ}$ , is :

<i>For Platinum-Iridium.</i>	<i>For Aluminium.</i>
$0\cdot000\ 008\ 600 + 0\ 000\ 000\ 002\ 28t$ or $10^{-9} (8600 + 2\cdot28t)$ .	$0\cdot000\ 022\cdot04 + 0\cdot000\ 000\ 010\ 6t$ , or $10^{-8} (2204 + 1\cdot06t)$ .

True coefficient of expansion at  $t^\circ$ , or mean coefficient between any two temperatures whose mean is  $t$ ;  $\alpha = \alpha + 2bt$ , is :

*For Platinum-Iridium.*

$$\alpha = 0.000\ 008\ 600 + 0.000\ 000\ 004\ 56t, \quad \alpha = 0.000\ 022\ 04 + 0.000\ 000\ 021\ 2t, \\ \text{or } 10^{-9} (8600 + 4.56t). \quad \text{or } 10^{-9} (2204 + 2.12t)$$

*For Aluminium.*

The amount of error introduced by the use of this aluminium compensator has been shown not to exceed  $\pm 0.02$  of an interference band, an amount less than the differences observed between the numbers of bands afforded by successive determinations under identical conditions.

In carrying out an actual determination, the interference apparatus having been adjusted for the production of an excellent field of bands, it is raised while the air bath is arranged on its annular support, and then lowered into position in the bath, and the latter is covered as described. The whole of this part of the apparatus about the second pedestal is arranged a couple of yards away from the first pedestal and its contents during these final adjustments preliminary to a determination, the movable lens on the eyepiece being fitted with its long distance tube, so as to focus the interference surfaces for the longer distance. This removes the heated part of the apparatus from the observing part during the determinations. All being finally adjusted, the reading of the inner bent thermometer is taken by a small cathetometer telescope near the first pedestal; the position of the interference bands at this initial temperature is then determined by measuring in drum readings the distance of the centre of reference, that of the little silvered ring, from the centre of the nearest band, if a band is not already actually centred, and by measuring also the distance between the two bands on each side of the centre. These two measurements enable the initial fraction of a band to be determined.

The temperature is then very slowly raised through the

first interval, to the neighbourhood of  $60^\circ$ , the bands being carefully counted one by one as they pass the reference centre; the permissible rate of rise of temperature depends largely on the number of bands to pass, and must be carefully controlled by the divided-quadrant gas tap, so that they never pass so quickly that they cannot be deliberately counted. When the level of temperature desired is reached it must be maintained constant for at least an hour, during which the bands should not move if all goes well. When this is so, the final fraction of a band can be measured, assuming that the last band has not stopped exactly over the reference centre. Thus the total number of bands corresponding to the interval of temperature employed will have been obtained. The temperature can then be allowed to rise further from this second level to the third and highest level, somewhere in the neighbourhood of  $120^\circ$ , and the number of interference bands which pass during this second interval of temperature determined in like manner to that for the first interval.

The observed number of interference bands and the fraction of a band, when multiplied by the half-wavelength of the light employed—generally red C hydrogen light  $0.0003281$  mm.—and corrected for change of wavelength due to the change of temperature and for any change of pressure in accordance with a formula given in the author's memoir, affords the exact measure of the alteration of the thickness of the air film, generally a diminution, under the reference spot, between the glass wedge-disc and the crystal or other object or the aluminium disc representing it. Knowing the coefficient of expansion of the platinum-iridium of the tripod screws, and also that of the aluminium of the cover disc, if one is used over the object, the only remaining unknown quantity—the expansion of the object under investigation—can readily be calculated.

The object in making the determination for two temperature intervals, or rather for three, as the sum of the first and second makes a third interval between the ordinary temperature and the upper limit, is to be able to determine not only the mean coefficient of expansion between two limits of temperature, but also the variation of the coefficient with change of temperature, as it is by no means a constant quantity, but varies regularly in accordance with a definite formula for the length,  $L_t = L_0(1 + at + bt^2)$  in which  $L_0$  is the length at  $0^\circ$  and  $L_t$  that at  $t^\circ$ , and whose constants  $a$  and  $b$  are different for different substances. It also enables the absolute coefficient of expansion  $a$  at any temperature  $t$  to be determined, as well as the increment of the coefficient per degree. For  $a = a + 2bt$ , and this expresses also the mean coefficient between any two temperatures the mean of which is  $t$ . The mean coefficient of expansion between  $0^\circ$  and  $t^\circ$  is, however, expressed by  $a + bt$ . A full discussion of the formulæ and the mode of making the calculations is given in the memoir on the dilatometer.<sup>1</sup>

With this dilatometer the coefficients of thermal expansion of the sulphates of potassium, rubidium, and caesium have been determined, for each of the three axial directions of the rhombic crystals of the three salts. Each of these nine quantities was determined either six or eight times, the results being remarkably concordant; altogether no fewer than sixty-four determinations were made, each occupying at least five hours. This allows an hour and a half for the rise of temperature through each interval, and an hour of constancy at each limit, during the whole of which time the bands were incessantly watched; for only by so doing can one be sure that no upsetting event, such as cracking of the crystal, occurs. The results themselves will be discussed in Chapter XIV. They were published in a second memoir.<sup>2</sup>

<sup>1</sup> *Phil. Trans.*, 1898, A, 191, 351.

<sup>2</sup> *Phil. Trans.*, 1899, A, 192, 455.

## CHAPTER IX

### THE ELASMOMETER.

THIS instrument extends the applicability of the interferometer to the determination of the coefficient of elasticity, by measuring the amount of flexure of a thin plate of the crystal or other substance to be investigated when pressed up into contact, near its ends, against a pair of platinum-iridium knife edges, by a known weight applied under its centre. The interferometer, consisting on one pedestal of the observing telescope, with its auto-collimator and attached hydrogen Geissler tube, and on the second pedestal of the suspended tube carrying the dispersing prisms above, to select the monochromatic rays employed, is the same as for the dilatometer. The first pedestal and its contents are mounted on a detachable plinth in front of the elasmometer, as will be gathered from the general illustration of the apparatus given in Fig. 13. The second pedestal is mounted on the back part of the iron base of the elasmometer itself, three toe plates being ready in position to receive the levelling screws of the pedestal tripod. When thus the interferometer is in position, the suspended tube of the second (back) pedestal may be brought by suitable rotation of the suspension arm centrally over the interference discs, the interference chamber which was attached for the purposes of the dilatometer having, of course, been removed and replaced by the cap fitted with the countervailing wedge. Thus far, we have the interferometer in its generally

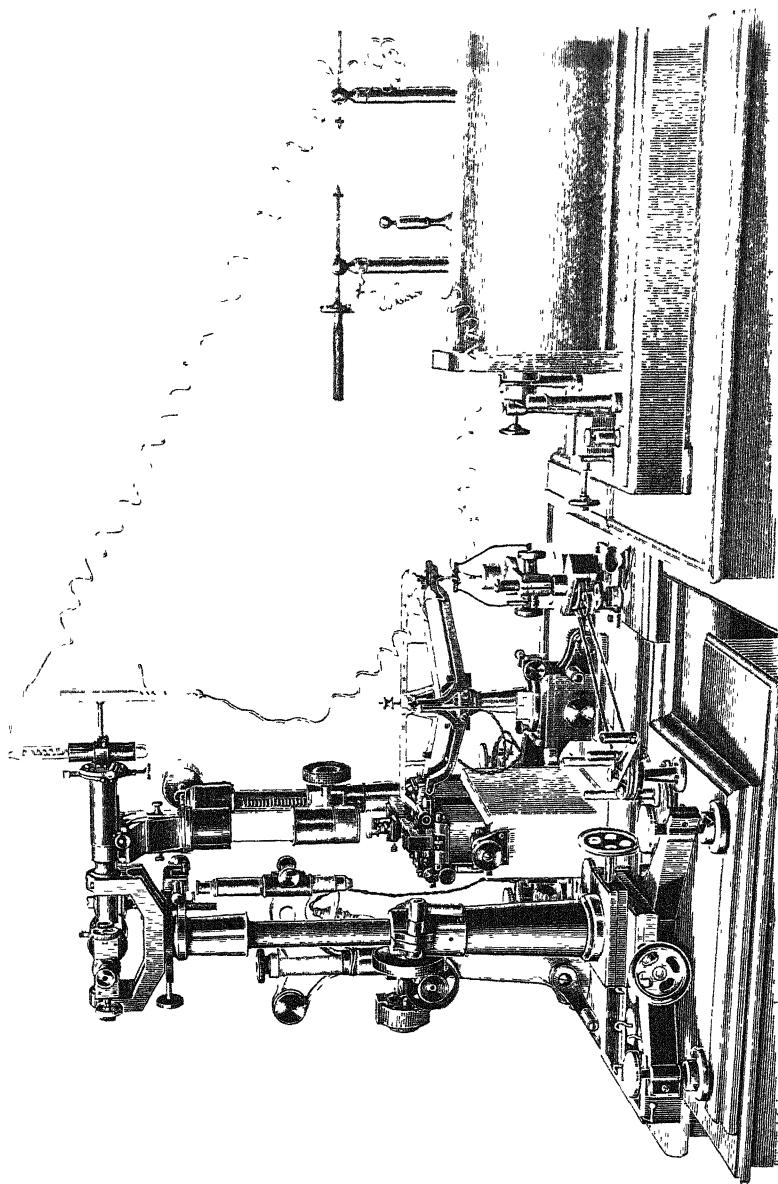


FIG. 13.—GENERAL ARRANGEMENT OF ELASMONOMETER AND INTENSIMETER

applicable form ; the rest of the apparatus is the elasmometer proper, which will now be described briefly. A full account of it will be found in the author's memoir to the Royal Society,<sup>1</sup> supplemented by some further additions described in a second memoir to the *Zeitschrift für Krystallographie*.<sup>2</sup>

The apparatus, although designed primarily for the investigation of the elastic properties of crystals, is the most accurate and convenient apparatus yet described for the determination of the elasticity constants of any and every solid substance whatsoever. Like the interferometer, dilatometer, monochromatic illuminator, and cutting-and-grinding goniometer, the instrument has been constructed by Messrs. Troughton and Simms, in a highly satisfactory manner.

The elasmometer proper is shown in its general aspect in Fig. 14. It carries its own interference tripod (seen slightly to the left and above the centre in Fig. 14), on which the colourless glass wedge-disc rests. It is seen even better in Fig. 15, which also shows the black-glass disc (just below the colourless one) which represents and moves with the crystal, being connected with and resting on the centre of the latter by an aluminium bluntly pointed rod, acting as the transmitter of the movement of the plate centre to the interference apparatus.

The elasmometer proper consists of the following seven essential parts :—

(1) A pair of platinum-iridium wedges, arranged with their edges downwards and parallel to each other, up against which the plate of the substance is to be bent by a weight applied under its centre through an upright agate point (slightly rounded and usually covered with a cone of white kid) standing up from the end of the balance beam, as shown withdrawn from position for

<sup>1</sup> *Phil. Trans.*, 1904, A, 202, 143.

<sup>2</sup> *Zeitschr. für Kryst.*, 1904, 39, 321.

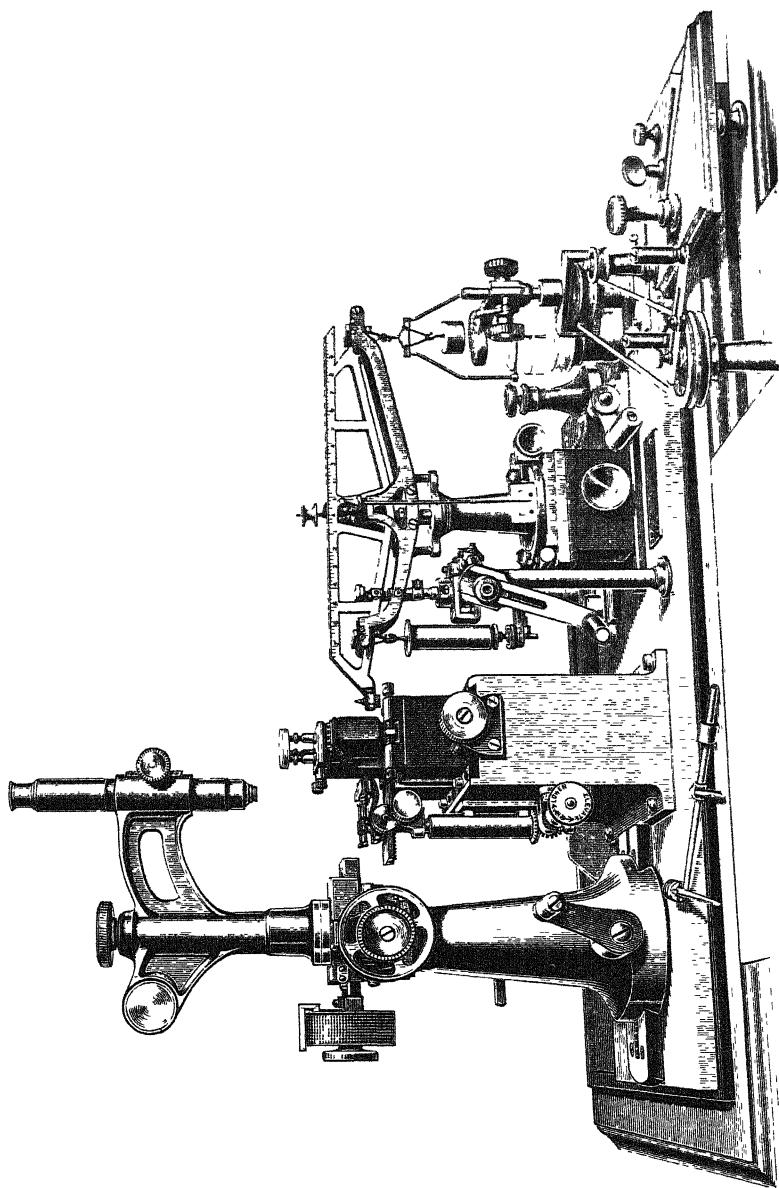


FIG. 14.—THE GLASSMOMETER PROPER.

the sake of clearness in Fig. 14, and in position in Fig. 15. The wedges are carried by a pair of gun-metal blocks in line with each other, which are adjustable as to their distance apart, and are suitably recessed at their inner ends, to accommodate (underneath the remaining overhanging portions) the wedges and the plate-supporting and weight-applying apparatus. They slide on a very rigid larger block of steel, mounted to the front and left

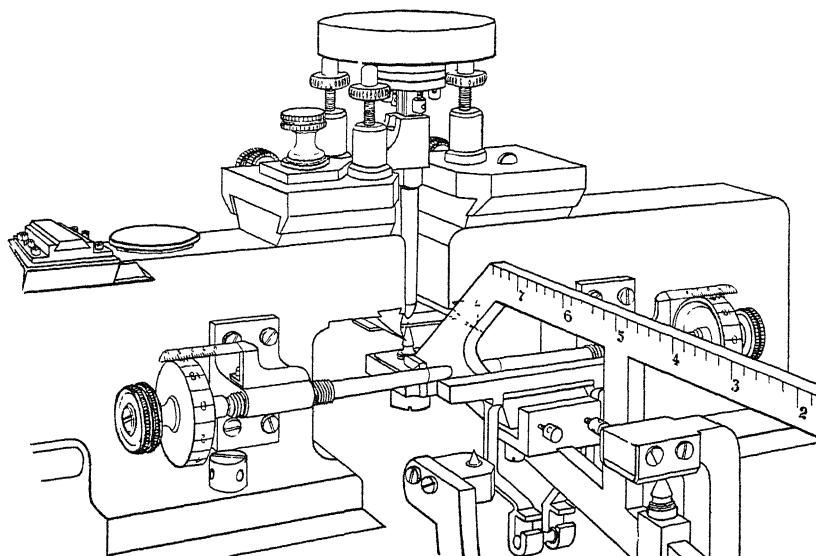


FIG. 15.—INTERFERENCE AND LOAD APPLYING APPARATUS OF ELASMOMETER.

of the centre of the iron base, and one of them is provided with fine adjustments for altitude and azimuth, to enable the knife edges to be set exactly parallel to each other.

(2) A pair of "mechanical fingers," for supporting the plate and adjusting it in the proper position under the knife edges, and for afterwards pressing it up into just full contact with them while the pressure-point of the balance beam-end is adjusted below the centre of the

plate. They are shown in Fig. 16. They are carried by a fitting to the left side of the steel block, as shown in Fig. 14, and terminate in little spring tables (shown separately to the right), each carrying a small gun-metal knife-edge above its inner side, and are adjustable for separation, height, and their position in or out of the recess. Delicate adjusting screws for moving (by pushing only) the plate in the two rectangular directions are also provided, the operation of which will be clear from Fig. 16.

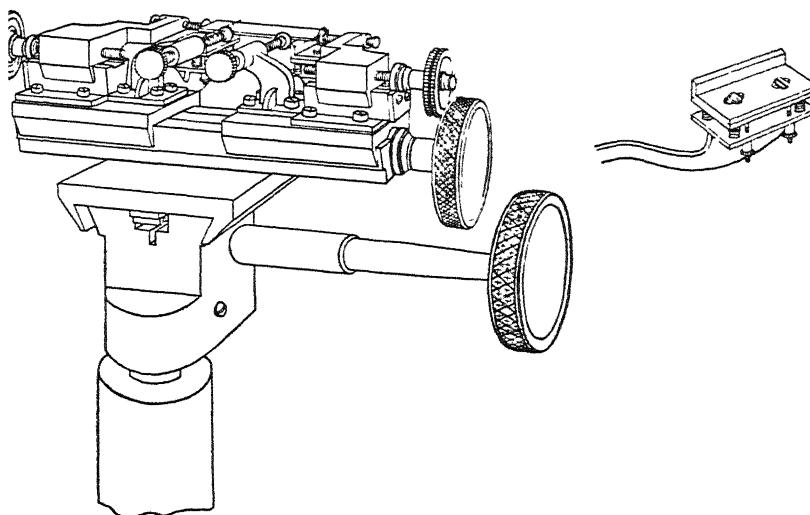


FIG. 16.—MECHANICAL FINGERS FOR ADJUSTING THE CRYSTAL PLATE.

(3) A delicate balance for weights up to 500 grammes, by Oertling, of special construction, at one end of the beam of which the bending weight is applied through the upright agate point already mentioned, the "pressure-point," which is carried instead of a pan at this end. Fig. 14 will render its construction clear. It is mounted to the right of the steel block on a strong base, which is movable by rack and pinion, so that the pressure-point can be exactly centred under the plate, that is under the centre of that portion of

the plate included between the knife edges against which it is pressed; an adjustment for azimuth is also provided in the mounting of the balance to aid in this object. A pair of delicate adjusting screws with graduated drum-heads and ivory tips, which are directed against the end of the balance beam near the pressure-point and from opposite sides of the beam, best seen in Fig. 15, are also mounted horizontally in the same straight line with each other, in bracket bearings screwed against the right side of each of the blocks. They not only enable the setting of the pressure-point to the plate-centre to be achieved deliberately and with certainty in the direction of the length of the object plate, acting as a fine adjustment to the azimuth adjustment of the balance itself already mentioned, but also enable the setting to be regained automatically if slightly deranged during a bending operation. For it is only necessary to record the drum-readings for the setting, afterwards withdrawing the screws adequately to permit of free movement of the beam, and then, after the bending operation is concluded, to reset the drums to their recorded readings, when the pressure-point will be returned to its centred position if not retained there.

A pan is suspended at the right-hand end of the beam, although the bending weight is not directly placed in it; the pan is convenient, however, for all preliminary tests and calibrations of the balance, and also useful for steady-ing purposes. Below it a second disc of aluminium is suspended by a short central rod, and immersed in cedar oil, which effectually and finally steadies the balance without impairing its sensibility, so that flickering of the interference bands, due to earth tremors, during the bending, which otherwise seriously interferes with the measurements, is absolutely avoided and prevented. Both pan and disc are counterpoised near the left end of the beam by a cylindrical counterpoise with platinised adjusting

weights, suspended from the usual Oertling agate plate and knife-edge fitting.

(4) A transmitter, for conveying the bending movement of the centre of the plate to the interference apparatus. It consists essentially of a vertically sliding aluminium rod, the lower bluntly-pointed end of which rests on the centre of the object plate, and the upper end of which is formed by the black-glass disc, carried in an adjustable manner, the upper surface furnishing one of the reflections which are caused to interfere to produce the bands. The portion of the rod just below the headpiece is of square section, with the sides of the square somewhat hollowed out, in order to obtain almost frictionless sliding in a correspondingly square boring in a carrier-fitting, attached by a screw with milled head to one of the blocks by means of a suitably shaped arm, the screw working in a slot which permits of accurate adjustment of the point of the aluminium rod over the plate centre.

This transmitter follows the bending of the plate at its centre absolutely, without the slightest hesitation or derangement of the interference bands, and quite as well on the lowering of the centre back again after bending as on its rising.

(5) An interference tripod for supporting the large colourless glass 35'-wedge-disc, bearing at the centre of its under surface the little silvered ring. One screw is mounted on the back block, and two screws are carried on the front block; the arm of the transmitter carrier passes between the two latter. The black-glass surface is arranged to be separated from the silvered-ring under surface of the wedge-disc only by a film of air, half a millimetre to a millimetre thick, just sufficient to allow for its diminution by the bending of the plate and consequent slight rise of the transmitter, without contact of the two surfaces being either imminent or possible.

(6) A measuring microscope, wherewith to determine

the dimensions of the plate and find its centre. It is mounted to the left of the steel block, and its two horizontal rectangular measuring movements provided with silver scales, read to a thousandth of a millimetre by a novel direct method. The subdivisions of the millimetre pitch of the screw are entirely afforded in each case by a large drum-head, the silver cylinder of which bears on its surface eleven equidistant circles parallel to each other and to the cylinder ends, the two outside ones being directly divided into 100 parts and joined by oblique lines affording the thousandths with the aid of an indicator. The pedestal supporting the microscope is adjustable by rack and pinion, manipulated by the lever shown in front in Fig. 14, along its basal bed at the position most convenient for the measurements, and thus capable of withdrawal out of the way when the microscope is to be replaced (over the interference tripod) by the interferometer suspended tube. Like the latter, the microscope is rotatable about the pedestal.

(7) A control apparatus, to enable the observer to modify at will the rapidity with which the bending force is applied, so as to retard adequately the transit of the interference bands and permit of their easy counting. This is most important, and indeed the whole success of the instrument is due to the effective way in which it is achieved. For if the weight were simply placed straight upon the pan, the bending would occur immediately and the whole number of bands would flash by instantly, with no possibility of counting them.

The control apparatus is situated at the right-hand end of the instrument and consists essentially of a tabular support for the loading weight, together with a relatively coarse rack and pinion adjustment and also an extremely fine screw adjustment for the height of the table about a supporting column. It is shown in Fig. 17, and in position in Figs. 13 and 14.

With the aid of the rack and pinion quick movement, manipulated by the two milled heads seen to right and left of the vertical stout shaft about which the table may be racked up and down, the weight—laid on the table near its further end, where it is broadened somewhat into a

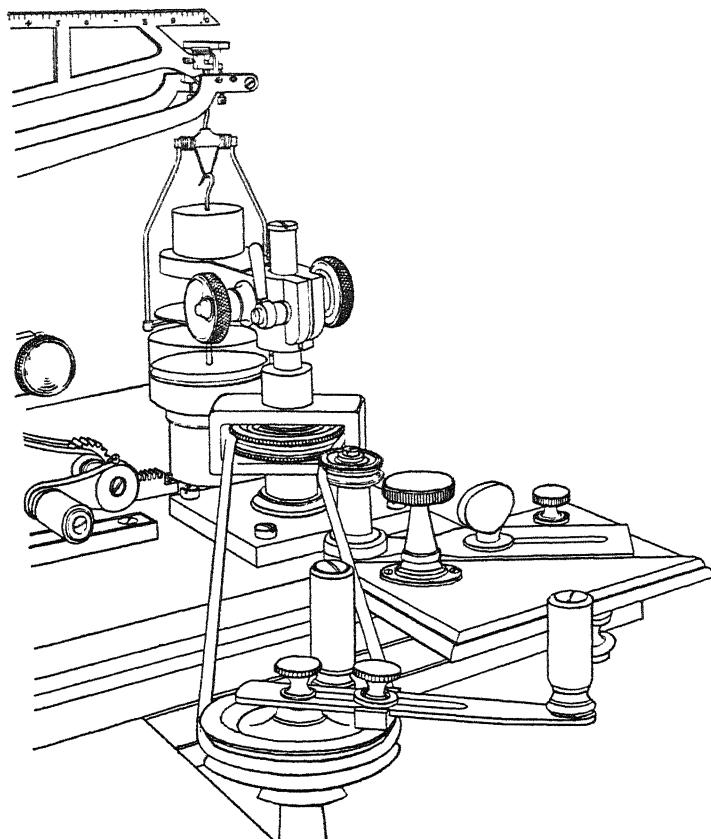


FIG. 17.—APPARATUS FOR CONTROLLING THE APPLICATION OF THE LOAD.

circular termination and covered with broadcloth to avoid injury to the platinised weights—can be lowered until its hook (all the platinised weights provided having hooks for the purpose instead of the usual knobs) all but rests in a

loop of strong but soft string, suspended from the top bar of the pan-frame. The weight can then, by manipulation of the fine movement, rendered still finer by the increasing tension of the string, be brought so slowly and regularly into action, resting eventually entirely in the loop, that the interference bands pass the centre of the silvered reference ring in the centre of the field of the eyepiece very slowly and deliberately and can be readily counted.

The important fine adjustment with which this is accomplished consists of a large driving-nut wheel, of which the central very fine screw thread engages with a corresponding screw of one-quarter millimetre pitch, which is cut for some distance along a convenient part of the shaft, rotation of the wheel thus causing the screw-shaft to move vertically. The driving wheel itself is restrained from vertical movement by its mode of mounting in a rigid frame solid with the short supporting column for the whole arrangement, within the cylindrical but keyed bore of which the shaft is capable of sliding without rotation. The pressure of an annular spring maintains the wheel with its lower boss pressed down on the floor of the box and prevents backlash. This fine motion is not effected by direct manipulation of the driving wheel, as this is too far from the observer watching the movement of the bands; but it is indirectly driven by a second wheel of the same size, 6 centimetres diameter, provided with a lever fitted with a vertical handle and adjustable for length, which at the maximum enables a driving radius of 9 centimetres to be secured if desired, thus affording an exceedingly fine control and adjustment for the bands. The two wheels are connected by a driving band of softened leather of circular section, the tension of which can be increased if desirable by the adjustable third pulley shown in Fig. 17 as pressing in the band on the right side. The driving wheel is mounted on a columnar bearing screwed down on the same accessory front basal

plinth as takes the interferometer telescope, and quite near to the pedestal of the latter, on the right. The accessory pressure pulley is mounted on a little separate base attachable in the convenient position at a moment's notice.

In carrying out a determination a small preponderance of weight is given to the pan side of the balance, in order that when the balance is released the pressure-point may press up against the centre, with just enough weight to keep the plate in full contact with the platinum-iridium knife-edges, when the gun-metal ones are withdrawn. The operation of bending the plate is thus always started with a small constant weight in action, and the plate very slightly preliminarily bent. It is the effect of the additional weights subsequently added from the control apparatus, in producing movement of the interference bands corresponding to further bending of the plate, that is to be measured. This small preliminary weight is effectively given to the pan end of the balance by merely removing the cylindrical counterpoise from the left side ; the weight of this is about 83 grammes, which, when the relative positions on the two arms of the balance is taken into account, is equivalent to a weight of 60 grammes on the pan, an amount of the right order to ensure effective contact of the plate with the platinum-iridium knife-edges.

The first actual load-weight may then be brought carefully into action, and a bending operation and the counting of the bands carried out as already described at the top of p. 82. They may then be recounted as the weight is again taken up by the table and as slowly removed from the loop and from operation, by the reverse motion of the driving wheel. The bands repass steadily and deliberately as before. The operations can be repeated as often as desired, the lateral screws for the fine adjustment of the pressure-point being employed between each pair of determinations, and then again withdrawn. After

the completion of the determinations for the first load, another higher weight is used, and a set of observations taken for it, and so on for as many different loads as one wishes to employ. The loads generally employed by the author are 100, 200, 300, and 400 grammes, and occasionally, if the plate will stand it, 500 grammes, the limit of the instrument.

The size of plate employed may be typically shown by quoting the dimensions of a plate of iron pyrites, one of several of this mineral which the author has been using for an investigation of its elasticity constants. Its length was 17.261 mm., its width 8.833 mm. and its thickness 0.875 millimetre. Other plates possessed similar lengths and thicknesses, but the width was successively greater than this, in order to test the effect of change in this dimension. The most suitable width, however, is about half the length. The constancy of the results for pyrites has proved to be remarkable; for each load the difference between the results of experiments carried out on successive days rarely reaches a tenth of an interference band.

## CHAPTER X

### GONIOMETRICAL RESULTS OF THE INVESTIGATION OF THE SERIES $R_2\frac{S}{Se}O_4$ AND $R_2M(\frac{S}{Se}O_4)_2 \cdot 6H_2O$ .

#### The Normal Sulphates and Selenates of the Rhombic Series, $R_2\frac{S}{Se}O_4$ .—It should be remembered that

the three alkali metallic elements potassium (at. wt. = 38.85 when H = 1), rubidium (at. wt. 84.9), and caesium (at. wt. 131.9) belong strictly to the same family group of the chemical elements, the first group in Mendeléeff's periodic table of the elements which has been given on p. 12, and to the even series, 4, 6, and 8, of that group. They are the most electro-positive of the elements. Indeed caesium is the most electro-positive of all the known elements. These three strictly analogous alkali metals, as was shown by Mitscherlich in his first research in 1819, are capable of being replaced by the radicle group  $NH_4$ , ammonium, without any apparent alteration of the crystalline form. They may also be similarly replaced by the peculiarly interesting metal thallium, discovered, owing to the striking green line in its spectrum, by Sir William Crookes in the year 1861. This element has double relations with the alkali group of metals, on one hand, forming similar compounds to those metals, and acting analogously as a monad metal, as if it truly belonged to the same family group; and with the aluminium group of triad metals on the other, to which latter group, three of the

periodic classification, it really belongs. In its first capacity it forms a sulphate,  $Tl_2SO_4$ , and a selenate,  $Tl_2SeO_4$ , exactly analogous to the sulphates and selenates of the three alkali metals proper, and its crystals are so very similar that they are included in the same isomorphous series. The point here to be emphasised, however, is that thallium does not truly belong to the same family group of the periodic system as potassium, rubidium, and cæsium, and we shall see that this distinction has important consequences. The atomic weight of thallium is 202.6.

**Solubilities of the Salts in Water.**—This essential difference between the thallium salts and the others of the series is immediately evident in regard to the degrees of solubility of the salts, which have a great influence on the ease with which the crystals may be grown. Slight solubility generally causes the rapid formation of small crystals, while a moderately good solubility is the most favourable condition for the production of well developed clear crystals. A very high solubility is generally accompanied by deliquescence of the crystals, and a crystallisation-retarding high viscosity of the saturated solution. The following table represents the number of grammes of the respective salts which are dissolved by 100 grammes of water at  $12^{\circ}C$ .—

*Solubility in Water at  $12^{\circ}$ .*

$K_2SO_4$	...	...	10 0	$K_2SeO_4$	...	...	...	115.0
$Rb_2SO_4$	.	...	42.0	$Rb_2SeO_4$	...	...	...	159.0
$Cs_2SO_4$	...	...	160.0	$Cs_2SeO_4$	...	...	...	245.0
$(NH_4)_2SO_4$	..	...	74.0	$(NH_4)_2SeO_4$	..	...	...	122.0
$Tl_2SO_4$	...	...	4.3	$Tl_2SeO_4$	.	...	.	2.4

It will be obvious from this table that the thallium salts are the least soluble of the series, and pronouncedly so. Also, that the general rule, according to which the selenate is more soluble than the sulphate, is not followed in the case of thallium selenate. Hence, these solubility results indicate the existence of some intrinsic difference between

thallium on one hand, and the alkali metals proper on the other.

The following law, however, is clearly indicated as regards the salts of the three alkali metals:—

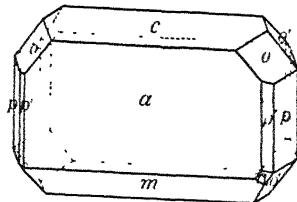


FIG. 18

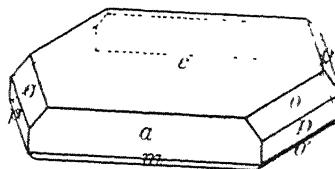


FIG. 19.

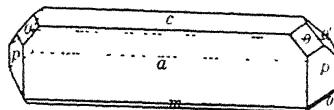


FIG. 20.

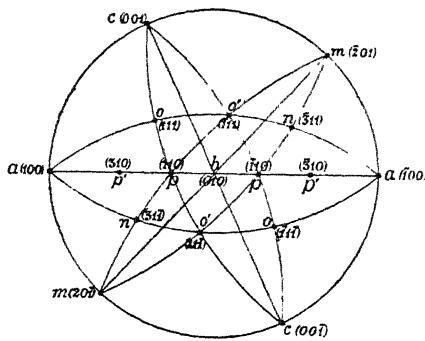


Fig. 21.

## CRYSTALS AND STEREOGRAPHIC PROJECTION OF MONOCLINIC AMMONIUM SELENATE.

The normal sulphates and selenates of potassium, rubidium, and caesium exhibit a progression in solubility which follows the order of the atomic weights of the three respective metals contained, the solubility becoming

greater as the atomic weight rises. The selenates are considerably more soluble in water than the sulphates, and, indeed, are deliquescent, particularly caesium selenate, the most soluble salt of the series; yet the progression according to atomic weight of the alkali metal is equally clear in both groups of salts.

**Dimorphism of Ammonium Selenate.**—Although the radicle ammonium,  $\text{NH}_4$ , behaves so much like an alkali metal as to produce a normal sulphate almost indistinguishable at first sight crystallographically from potassium sulphate, and which will be shown to be placed on good grounds in the same isomorphous series, as originally suggested by Mitscherlich, still the essential difference between a true alkali metal and such a radicle-group of the atoms of two different elements is at once apparent when we come to the selenate. For on preparing this salt by passing ammonia gas into pure dilute selenic acid, the crystals, which are excellently developed and about which no possible crystallographic doubt can arise, prove to be altogether different from the other salts of the series, and to belong to the monoclinic system instead of to the orthorhombic system. Three typical crystals are shown in Figs. 18, 19, and 20, and the stereographic projection in Fig. 21.

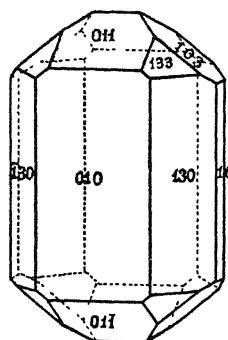


FIG. 22.—RHOMBIC AMMONIUM SELENATE.

A rhombic form of ammonium selenate was once, in the year 1862, obtained by von Hauer and described by von Lang, and the appearance of one of these crystals is shown in Fig. 22.

This historic specimen was most kindly sent to the author from Vienna by Prof. von Lang, and in spite of some little deliquescence during the intervening forty-four years, the crystals still afforded measurements which amply confirmed those of 1862 as to the system, angles, and optical

characters. Von Lang also mentioned some acicular crystals in his original memoir, and some of these were present in the specimen bottle sent from Vienna, and they prove to be identical, although very small and elongated in the mode of their development, with the author's monoclinic form. These needles were found to be almost pure selenate of ammonium, but the rhombic crystals contained admixed ammonium sulphate, which entirely explained their formation. For the author has obtained rhombic mixed crystals of ammonium selenate with ammonium sulphate,

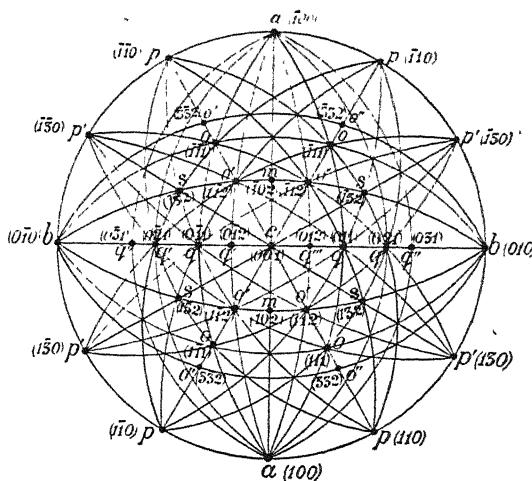


FIG. 23.—STEREOGRAPHIC PROJECTION OF RHOMBIC SERIES.

potassium selenate, and rubidium selenate respectively. and in the case of the admixture with the last-mentioned salt any particular individual crystal contained as much as 60 per cent. of ammonium selenate. Hence, there can be no question about the fact that ammonium selenate is dimorphous, occurring in both a rhombic form isomorphous with the sulphate and with the whole series under consideration, and in a monoclinic form. The latter is the one to which the ordinary conditions of temperature and pressure lend themselves most favourably, hence it is the

common form. The rhombic form is as yet only known in mixed crystals, and it would appear that a small

## THE SULPHATES OF THE ALKALIES.

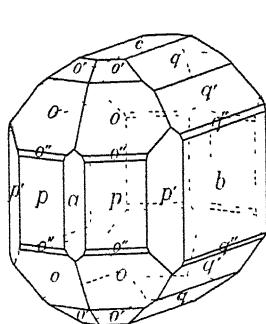


FIG. 24.— $K_2SO_4$ .

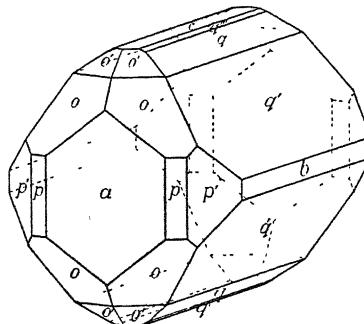


FIG. 25.—Rb<sub>2</sub>SO<sub>4</sub>.

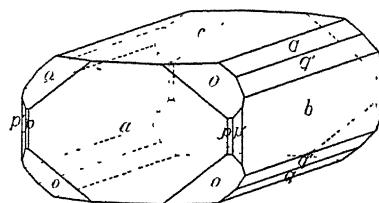


FIG. 26 —  $\text{Cs}_2\text{SO}_4$ .

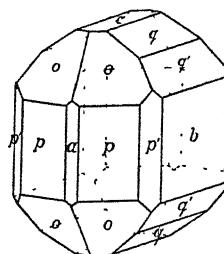


FIG. 27.— $(\text{NH}_4)_2\text{SO}_4$ .

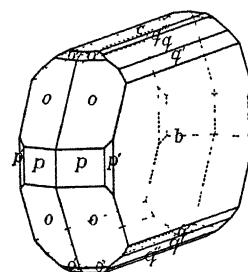


FIG. 28.— $Tl_2SO_4$ .

percentage of admixed ammonium sulphate is sufficient to induce the salt to take up the rhombic form.

The General Crystallographic Characters of the Rhombic Series  $R_2SeO_4$ .—The general stereographic projection for the whole series is given in Fig. 23, and the succeeding nine illustrations pourtray the appearance of typical crystals of the nine salts other than ammonium

THE SELENATES OF THE ALKALIES.

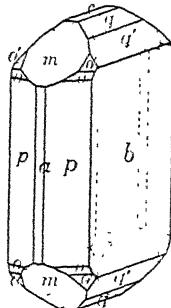


FIG. 29.— $K_2SeO_4$ .

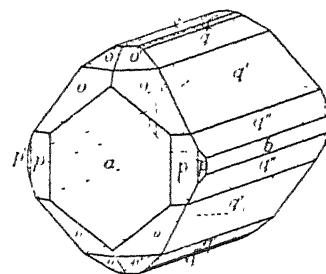


FIG. 30.— $Rb_2SeO_4$ .

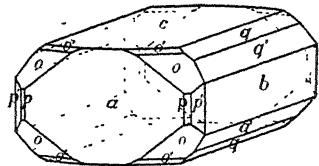


FIG. 31.— $Cs_2SeO_4$ .

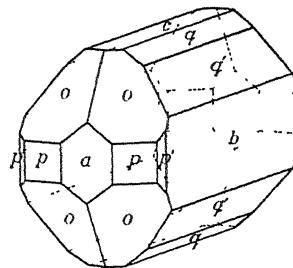


FIG. 32.— $Tl_2SeO_4$ .

selenate. The name of each crystal is given under the drawing.

The whole of the salts crystallise magnificently, and are eminently suitable for goniometrical investigation. The selenates are somewhat hygroscopic, particularly caesium selenate, but by using a larger number of individual crystals, about twenty-five being employed, and selecting

only dry weather for the measurements, storing the crystals meanwhile in small bottles kept in a desiccator, the usual large number of measurements were eventually carried out without appreciable deliquescence; as soon as any sign of it became evident, the crystal was discarded.

The faces developed on the crystals were chiefly the three pinakoids, the macropinakoid  $a = \{100\}$ , the brachypinakoid  $b = \{010\}$ , and the basal pinakoid  $c = \{001\}$ ; the primary prism  $p = \{110\}$ , and another prism  $p' = \{130\}$ ; the primary pyramid  $o = \{111\}$  and a secondary one  $o' = \{112\}$ ; and the brachydomes  $q = \{011\}$  and  $q' = \{021\}$ . The remaining forms shown on the stereographic projection were rarer, and particular ones were characteristic of certain crops of specific salts.

The crystals have a very marked pseudo-hexagonal habit, that is they closely resemble hexagonal crystals in the angular disposition of the faces. Thus, for instance, the angles of the prism zone are almost exactly  $60^\circ$  and  $30^\circ$ ; the angle  $bp = \{010\} : \{110\}$  in potassium sulphate is  $60^\circ 12'$ , and the angle  $pp' = \{110\} : \{130\}$  is actually  $30^\circ 0'$ . The value of the angle  $bp$  varies a few minutes in the

other alkali metallic salts of the series, and about three-quarters of a degree in the case of the thallium salts, but never reaches  $61^\circ$ . In some cases, as in that of a crystal of rubidium sulphate shown in Fig. 33, the crystals resemble hexagonal pyramids so closely that they might well be mistaken for such. That they are really orthorhombic is, of course, proved by the exact measurement of the angles, and fully confirmed by the optical properties, which are those of a clearly biaxial crystalline substance.

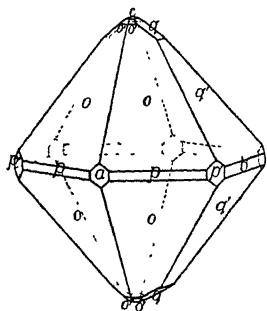


FIG. 33.— $\text{Rb}_2\text{SO}_4$ .

This curious property of adopting a pseudo-hexagonal

habit is further emphasised by the marked prevalence of repeated twinning in the form of triplets of hexagonal section, which has long been known to be a characteristic property of potassium sulphate, and has been shown by the author to be observed frequently in the cases of several other salts of the series. Two characteristic triplets, for instance, of potassium selenate are shown in Figs. 34 and 35. In the first of these interpenetration is complete, and

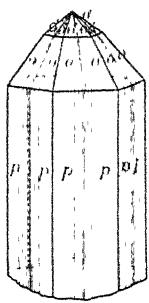


FIG. 34.

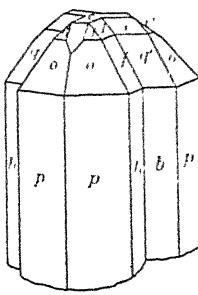


FIG. 35.

the resemblance to a hexagonal prism terminated by a hexagonal pyramid is all but perfect. Each face is composed of two halves, however, inclined at a few minutes angle, corresponding to the angular deviation from  $60^\circ$ . In the second example, Fig. 35, the interpenetration is less complete, and a prism of cruciform section is produced.

**Comparison of the Exterior Angles of the Rhombic Series  $R_2SeO_4^S$ .**—A complete list of the angles of the nine rhombic salts of the series is given in the accompanying table. It embodies the whole of the results of the goniometrical measurements, and is arranged in comparative fashion, so that by following a horizontal line with the eye, the change in magnitude of any one and the same angle, as one element or base is replaced by

## COMPARATIVE TABLE OF INTERFACIAL ANGULAR MAGNITUDES

another, can be seen at once. It is followed by a second table in which the results are analysed in a very con-

## AVERAGE AND MAXIMUM ANGULAR CHANGES.

Salts compared	For replacement of	Average change	Maximum change
$K_2SO_4$ and $Rb_2SO_4$ ..	$K$ in $K_2SO_4$ by rubidium ..	0 9	0 24
$K_2SO_4$ and $(NH_4)_2SO_4$ ..	“ ammonium ..	0 14	0 37
$K_2SO_4$ and $Cs_2SO_4$ ..	“ caesium ..	0 16	0 41
$K_2SO_4$ and $Tl_2SO_4$ ..	“ thallium ..	0 26	1 16
$(NH_4)_2SO_4$ and $Tl_2SO_4$ ..	$NH_4$ in $(NH_4)_2SO_4$ by thallium ..	0 14	0 39
$Rb_2SO_4$ and $Tl_2SO_4$ ..	$Rb$ in $Rb_2SO_4$ by thallium ..	0 25	1 10
$Cs_2SO_4$ and $Tl_2SO_4$ ..	$Cs$ in $Cs_2SO_4$ by thallium ..	0 27	1 2
$Rb_2SO_4$ and $(NH_4)_2SO_4$ ..	$Rb$ in $Rb_2SO_4$ by ammonium ..	0 20	0 53
$Cs_2SO_4$ and $(NH_4)_2SO_4$ ..	$Cs$ in $Cs_2SO_4$ by ammonium ..	0 25	1 10
$K_2SeO_4$ and $Rb_2SeO_4$ ..	$K$ in $K_2SeO_4$ by rubidium ..	0 11	0 36
$K_2SeO_4$ and $Cs_2SeO_4$ ..	“ caesium ..	0 17	0 56
$K_2SeO_4$ and $Tl_2SeO_4$ ..	“ thallium ..	0 27	1 21
$Rb_2SeO_4$ and $Tl_2SeO_4$ ..	$Rb$ in $Rb_2SeO_4$ by thallium ..	0 26	1 5
$Cs_2SeO_4$ and $Tl_2SeO_4$ ..	$Cs$ in $Cs_2SeO_4$ by thallium ..	0 27	1 6

venient manner, affording a concise demonstration of the nature of the angular changes which occur on passing from one salt to another. It shows in the third column the average change for each metallic or basal replacement, that is, the arithmetical mean of all the angular differences between the potassium salt, considered as the first member of the group, and the salt in question, or between any two other salts of either group, ignoring the sign of the change, that is, whether the angle has increased or diminished. In the fourth column the maximum change is appended in each case.

The three sulphates of potassium, rubidium, and caesium may first be compared among themselves, and also the three selenates of these metals with one another. We observe at once that the whole of the morphological angles of the crystals of the rubidium salt of either the sulphate or the selenate group are without exception intermediate in value between the analogous angles on the crystals of the potassium and caesium salts of the same group.

The differences between corresponding angles of the three salts are very small, rarely attaining twenty minutes of arc for the passage from the potassium to the rubidium salt of the same group, or from the rubidium to the cæsium salt, and the maximum change for the direct passage from the potassium to the cæsium salt of one and the same group never reaches a degree.

The intermediate position assumed by the rubidium salt is somewhat nearer to that of the cæsium salt than to that occupied by the potassium salt.

It is evident, therefore, that change of atomic weight of the alkali metal is accompanied by a corresponding change in the magnitudes of the exterior interfacial angles of the crystals, the progressive change in the atomic weight from potassium through rubidium to cæsium, or *vice versa*, being invariably accompanied by a similarly progressive change in the angles. The exterior interfacial angles of the crystals are, therefore, a function of the atomic weight of the alkali metal, the function being such as produces a diminishing effect as the atomic weight rises higher and higher.

The change of sulphur for selenium, or *vice versa*, in a potassium, a rubidium, or a cæsium salt produces a similar effect, a small change in the crystal angles occurring which rarely attains twenty minutes of arc. Moreover, in general, the angular change is of the same sign, whichever one of the five bases is present in the salt in which sulphur is replaced by selenium. But the sign is the opposite of that for the replacement of a lighter by a heavier metal. That is, change of atomic weight produces opposite effects on the crystal angles according as it occurs in the positive or in the negative element.

What is of the highest importance in the above results is, that the changes of angle on passing from a potassium salt to a rubidium or a cæsium salt occur in the same direction, according to the regular law of progression with

atomic weight of the alkali metal which has just been pointed out. This cannot be too clearly emphasised, for it is only in the cases of these three truly homologous members of the same exclusive family group of the alkali metals—potassium, rubidium, and caesium—that this is true.

As regards ammonium sulphate, it will be observed that small angular changes of a similar order of magnitude are introduced by the replacement of potassium by ammonium, the extent, as regards either the average or the maximum change, being greater than when potassium is replaced by rubidium, but less than when it is replaced by caesium. But the direction of the change shows no rule, for out of the thirty-seven angles compared, twenty-four exhibit a change in the contrary sense to that which occurs when potassium is replaced by either rubidium or caesium, ten show a change in the same direction, and three angles remain unchanged.

Hence there is a great difference apparent between the three alkali metals and the radicle ammonium, obviously due to their different constitution, namely, elements on one hand belonging strictly to the same family group, and a radicle group,  $\text{NH}_4$ , on the other, which happens to have alkaline, strongly basic, properties like the alkali metals, and the same effective monadic valency. It is thus capable of replacing these metals in their sulphates or selenates without altering the crystal system or even class, and, as we have seen, with less alteration of the angles than is observed when the strongest of these metals in electro-positive properties—caesium—replaces the relatively weakest, potassium. But the direction of the change of angle is promiscuous, and certainly bears no relation to the regular law which, we have seen, governs the angular changes of the three definitely progressively related alkali metals.

As regards thallium, a very similar result was obtained,

as will be clear from a consultation of the table of angles in the cases of both the sulphate and the selenate of thallium. It is at once apparent that the angles are precisely analogous to those for the sulphates and selenates of the alkali metals, and sufficiently close to warrant the inclusion of thallium sulphate and selenate in the same isomorphous series with those salts—giving the term “isomorphism” the broad signification now assigned to it by the author so as to admit such relatively minute changes of angle as are here observed. Yet, while this is so, the angular changes introduced by the replacement of potassium by thallium in the sulphate and selenate are considerably greater than those brought about by the replacement of potassium by either rubidium, cæsium, or ammonium.

It will be clear from the instructive table of average and maximum angular changes that both these quantities are one and a half times as much when thallium replaces potassium as when cæsium replaces potassium in either sulphate or selenate, and three times as much in the sulphate group, or two and a half times in the selenate group, as when rubidium replaces potassium. They are also twice as much when thallium replaces potassium in the sulphate as when ammonium replaces potassium. In short, the changes brought about by the introduction of thallium are nearly twice as great as the maximum changes effected by interchanges of the true alkali metals among themselves in the salts of the series.

The actual amount of the average angular change for the replacement of potassium by thallium is proportional to its atomic weight, when compared with the average change brought about by replacing potassium by cæsium. The two amounts are  $16'$  and  $26'$  in the sulphate group, and  $17'$  and  $27'$  in the selenate group. The atomic weights of cæsium and thallium being  $131.9$  and  $202.6$  respectively, if we calculate the effect of a metal of the

latter atomic weight on the assumption that one of the former atomic weight produces 16' or 17', we find it to be 25' or 26', only a single minute different from the observed amount of angular change for the introduction of thallium. But, just as was observed for ammonium, the direction of the change is promiscuous, sometimes being the same as when rubidium or caesium replaces potassium, and sometimes in the contrary direction, no law governing the sign of the change.

Hence, as in the case of ammonium, the different chemical nature of the element thallium, as compared with the alkali metals proper, is strikingly displayed in the small but extremely interesting and important changes in the interfacial angles of the crystals which accompany the replacement of one of those bases by another in the isomorphous series.

The difference of angle between the sulphate and the selenate of thallium is relatively very small, as was shown to be the case also with respect to the pairs of analogous salts of the two acids sulphuric and selenic respectively in which the bases were potassium, rubidium, and caesium. The average change of angle occurring when the sulphur in thallium sulphate is replaced by selenium is 11', and the maximum change is 30'.

**The Double Sulphates and Selenates of the Monoclinic Series  $R_2M(\frac{S}{Se}O_4)_2 \cdot 6H_2O$ .**—As stated in Chapter IV., that group of the salts of this series in which the *M*-metal is zinc will be taken as a type of the whole series, inasmuch as the results for all the groups, so far as they have been completed up to date (and types of all have now been investigated), indicate absolutely the same general facts. We shall, therefore, take the zinc group as a type of the whole of the eight groups in which, besides zinc, the other *M*-metals are magnesium, iron, nickel, cobalt, manganese, copper, and cadmium. The ten salts of the zinc group

are those containing either zinc sulphate or zinc selenate combined with one (containing the same acid) of the nine simple salts just considered of the series  $R_2\frac{S}{Se}O_4$ , and with ammonium selenate; the latter, in spite of its dimorphism, forms the double salts with *M*-selenates quite as readily—indeed, often with greater facility—as the nine simple salts which normally form only rhombic crystals.

The stereographic projection common to the whole monoclinic series,  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ , is given in Fig. 36. The whole of the forms indicated on it are rarely developed

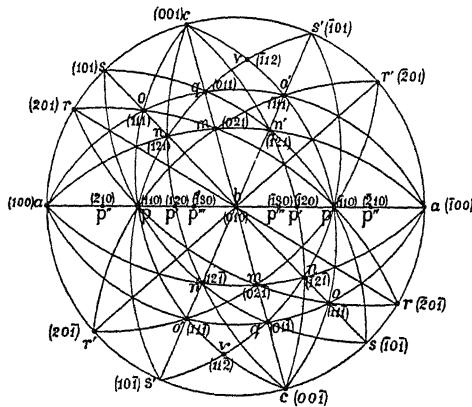


FIG. 36.—STEREOGRAPHIC PROJECTION OF MONOCLINIC SERIES.

on one and the same crystal, but this has happened in a few cases of crystals extremely rich in faces.

## Characteristically Progressive Habits of the Salts containing the Three Alkali Metals Proper.

—One of the most interesting results derived from the investigation of this series is that a regular variation in the “habit” of the crystals of the salts containing potassium, rubidium, and caesium respectively is observed. There was a decided tendency for something of this sort in the rhombic series, but the great diversity of habit

shown by growth in different circumstances in that series masked it as a rule. But in this monoclinic series there is no mistaking the phenomenon. It will be rendered clear by Figs. 37, 38, and 39, which represent typical crystals respectively of a potassium salt, a rubidium salt, and a caesium salt. The faces of the principal forms,  $c=\{001\}$  the basal pinakoid,  $p=\{110\}$  the primary prism, and  $q=\{011\}$  the primary elino-prism, show a marked and definite progression in development in the three salts, any one of them on the rubidium salt being developed to an intermediate extent compared with its development on the potassium and caesium salts.

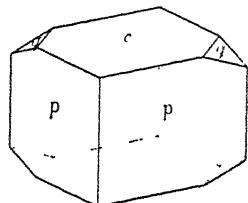


FIG. 37.—K-Salt.

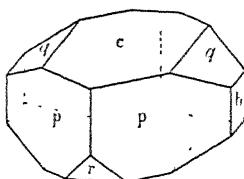


FIG. 38.—Rb-Salt.

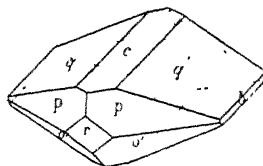


FIG. 39.—Cs-Salt.

These illustrations in Figs. 37, 38, and 39, besides showing the representative types of the salts of the three alkali metals proper, are the actual reproductions of the drawings made from real crystals of potassium-zinc, rubidium-zinc, and caesium-zinc sulphates employed in the goniometrical measurements. In the next three figures are given similar reproductions of drawings made at the time of the measurement of the three corresponding selenates containing zinc and respectively potassium, rubidium, and caesium. It will be seen at once that the characteristic types are clearly reproduced in these selenates, the only difference being the addition of the secondary faces, the primary faces bearing their characteristic relationships.

The ammonium and thallium salts crystallise in habits closely resembling on the whole the rubidium salts, indeed Fig. 41, with the exception of the  $p'$  and  $n$  faces, stands

just as truthfully for thallium zinc sulphate and selenate as for rubidium zinc selenate. The ammonium salts occasionally, however, exhibit habits resembling those of the potassium and caesium salts.

The salts of this monoclinic series are notable for the magnificent development of their crystals. Some members of the group have been grown as large as an inch in diameter, while retaining absolute homogeneity, transparency, and exceptional planeness and brilliance of the faces. Indeed, it is quite easy to prepare crystals of many of the salts of this series, especially the selenates, large enough for lantern demonstration work, particularly for the preparation of large section-plates suitable for use with the lantern polariscope.

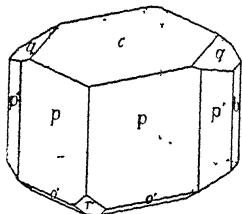


FIG. 40.—KZn Selenate.

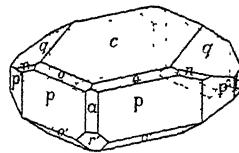


FIG. 41.—RbZn Selenate.

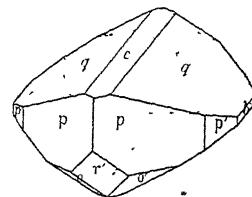


FIG. 42.—CsZn Selenate.

**Comparison of the Exterior Interfacial Angles of the Ten Salts containing Zinc.**—In the accompanying table A are presented comparative lists of angles, the salts being arranged in the order of the *R*-metals as given in the previous table representing the results for the rhombic simple salts of those metals. The ammonium salts are of course included, both sulphate and selenate; for, as already pointed out, ammonium selenate forms a monoclinic double salt with zinc selenate and six molecules of water just like the others, so that we can here compare the ten salts, two groups of five each, containing respectively sulphuric and selenic acids.

Considering first the relations between the salts contain-

TABLE A.—Comparison of the Augular Magnitudes.

been completed so far as all these salts of both acids are concerned, and of all the other sulphate groups.

As regards the position of ammonium and thallium, the replacement of potassium by ammonium, in all but two and four cases respectively out of the 36 angles compared in the zinc sulphate and zinc selenate groups, and that of thallium in all but three cases in each group, is observed to occur in the same direction as when potassium is replaced by rubidium or caesium. But the amount of the change in the case of the replacement of potassium by ammonium is much larger than accompanies the replacement by rubidium, and is usually either nearly as large as, or slightly larger than (in the magnesium selenate group), when potassium is replaced by caesium. In the case of the replacement of potassium by thallium, the amount of either the average or maximum change is intermediate between that produced by substituting rubidium and caesium respectively for potassium. These facts are concisely expressed in table C, and more closely analysed in table D.

TABLE D.—*Analysis of Thirty-six Angles of Ammonium and Thallium Salts.*

Group	No. in which change is " in same direction as on replacing K by Rb or Cs		No. of those in col. 2 in which change is greater than for replacement of K by Rb		No. of those in col. 3 in which value of angle lies				
					Between values for Rb and Cs salts, but nearer to Rb		Between values for Rb and Cs salts, but nearer to Cs.		Outside value for Cs salt
	NH <sub>4</sub>	Tl.	NH <sub>4</sub>	Tl.	NH <sub>4</sub>	Tl.	NH <sub>4</sub>	Tl.	
Zn sulphate series ...	34	33	31	24	5	14	18	6	8
Zn selenate , ,	32	33	29	25	6	10	11	7	12
									4
									8

The effect of replacing sulphur by selenium is to produce angular changes of the same order as those occurring when the alkali metal is changed, and it is noteworthy that they

are generally of the same sign into whichever sulphate the selenium is introduced.

For instance, the obtuse axial angle is always diminished when sulphur is replaced by selenium. But, as in the case of the simple salts, the sign of the change is opposite to that which is observed when a lighter is replaced by a heavier alkali metal.

**Comparison of the Axial Ratios of both Series.**—The crystallographic axial ratios for our typical zinc group of the monoclinic double salt series are compared in table E, and those for the simple salt rhombic series in the

TABLE E.—*Morphological Axial Ratios.*

Salt	Ratios of Axes.		
	<i>a</i>	<i>b</i>	<i>c</i>
Potassium zinc sulphate . . . . .	0·7413	1·0	5044
Rubidium „ „ . . . . .	0·7373	1·0	5011
Ammonium „ „ . . . . .	0·7368	1	0·4997
Cæsium „ „ . . . . .	0·7274	1	0·4960
Thallium „ „ . . . . .	0·7413	1	0·5010
Potassium zinc selenate . . . . .	0·7458	1·0	5073
Rubidium „ „ . . . . .	0·7431	1	0·5019
Ammonium „ „ . . . . .	0·7409	1	0·5040
Cæsium „ „ . . . . .	0·7314	1	0·4971
Thallium „ „ . . . . .	0·7479	1	0·5022

table on page 119 of the next chapter. Two facts are at once apparent, namely, that the ratios of the rubidium salt of each group are intermediate between those of the potassium and cæsium salts, but that also the changes are of a remarkably slight character.

The author has fully investigated the reason for this smallness of the changes brought about in this crystallographic element by interchange of the mutually replaceable alkali metals, and so long ago as in his 1893 memoir on the double sulphates, page 356, it was concluded that: "No indication of the full nature of the change brought about on replacing one metal by another in such an isomorphous series is afforded by a comparison

of the axial ratios, as simultaneous changes, which more or less neutralise each other, occur in the inclinations of the planes which determine them. The angles themselves alone furnish complete information concerning the change of external form."

In addition to this cause it will be seen in the next chapter that there is a still more fundamental reason why the axial ratios do not afford any very valuable comparative information as to the structural dimensions of the crystals of the various salts of an isomorphous series. But it is certainly interesting that, even with these large limitations, the axial ratios do still exhibit a progression, though only of a minute character, in the order of the atomic weights of the alkali metals.

As regards the position of the ammonium\* and thallium salts with respect to the axial ratios, all that can be said is that the values of the ratios for these salts are such as entitle them to be placed in the same isomorphous series with the analogous salts of the alkali metals potassium, rubidium, and cæsium.

## CHAPTER XI.

### THE VOLUME RELATIONSHIPS OF THE SIMPLE AND DOUBLE SULPHATES AND SELENATES, AND THE CONCEPTION OF MOLECULAR DISTANCE RATIOS.

THE crystallographic element referred to at the close of the last chapter, and known as the "ratio of the axes," so useful from the restricted point of view of the particular crystallised substance under investigation, as indicating immediately the relative lengths of the three crystallographic axes cut off by the fundamental primary pyramidal face (111), is, as will be seen from table E of these ratios given at the close of the last chapter, and from the further one given on page 119, usually expressed in terms of the length of the axis  $b$  taken as unity, that is, as  $a : 1 : c$ . While admirable for its specific purpose, that of the crystallographic description and definition of the substance in hand, such a series of ratios for this one substance is obviously not strictly comparable with that for any other, if we desire to represent the *relative dimensions* of the two substances along the axial directions in space. For one of the quantities,  $b$ , being unity, is always the same.

Now of one thing we are absolutely certain, that whatever the structure of the members of an isomorphous series may be—confining our meaning for the present to such a series in the strictest sense, formed by the interchange of elements belonging exclusively to the same family group of the periodic classification, such as the

three alkali metals under consideration, potassium, rubidium, and cæsium—that structure is similar for all the members of the series, the same type of space-lattice being present in all. Hence, the units of these space-lattices of the various salts of the series, the elementary parallelepipeda, will be fairly and truly comparable with each other. Whether those of other less exclusive members of the isomorphous series, such as the salts containing ammonium and thallium, are also equally comparable is a matter for discussion, which will be referred to later. But we are on uncontroversibly safe ground when we accept it as a fact that the space-lattices of the structures of the potassium, rubidium, and cæsium members of the series are constructed on the same plan, and that the elementary parallelepipeda, the molecular structural units, are of similar shape and character, and differ only in their absolute and relative dimensions. But any comparison of the members of different series is as yet a matter for the future, although there are indications that we are approaching the time when such will be possible by the introduction of an additional correlating factor, beyond the known factors which we shall now proceed to discuss.

From the foregoing it will at once be obvious that the crystallographic axial ratios do not afford us the desired comparative dimensions of the structural-unit parallelepipeda. But they do afford us the relations of the three space dimensions for that one substance for which they were calculated, and it will be obvious that if there were some other factor available which would give us the relations of the volumes of the parallelepipeda of the several salts of the series, we could derive the three relative spacial dimensions by combining the two factors. Such a volume factor we fortunately do possess, in the long misunderstood but most valuable constant—now it is understood—molecular volume. This is the physical

constant so usefully employed by Kopp in the case of liquids, and is afforded by the quotient of the molecular weight of the substance by its specific gravity. We have now learnt to appreciate the fact that molecular volume can only be applied for comparative purposes, in the cases of solids, when we are certain that the internal structure of those solids is similar and strictly analogous. In an isomorphous series like that afforded by any group of salts of the alkali metals potassium, rubidium, and cæsium, we have, however, just these ideal conditions for the valid comparison of the molecular volumes.

In the year 1893, about the time of the publication of the author's memoir on the goniometry of the monoclinic double sulphates, F. Becke of Prague<sup>1</sup> suggested this combination of the molecular volume with the crystallographic axial ratios, to produce a new series of relative spacial ratios. In a very friendly letter Prof. Becke communicated his idea to the author, who at once saw its value and applied it to arrive at the spacial dimensions of the structural units of the rhombic sulphates of potassium, rubidium, and cæsium, and published an account of the results in the 1894 memoir<sup>2</sup> on those salts, giving every credit to Becke for his idea. The author termed the new ratios "distance ratios." For they express the relative distances separating the points of the space-lattice, the analogous points representing the chemical molecules, along the directions of the crystallographic axes. It is inaccurate to regard them as indicating the actual dimensions in space of the chemical molecules themselves, for we do not yet know how much of the space defined by the elementary parallelepipedon is occupied by real matter and how much is free space, or ether-occupied space. The author has since had reason to add the word "molecular" to the title of the ratios, and there can be no question that

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<sup>1</sup> *Anzeiger der Kais. Akad., der Wiss., Wien*, 1893, **30**, 204.

<sup>2</sup> *Journ. Chem. Soc.*, 1894, **65**, 658.

the most suitable term for them, at once expressive of their real meaning and nature, is "molecular distance ratios."

Just before the appearance of the author's 1894 paper, however, a memoir was published by Muthmann<sup>1</sup> in which Becke's idea, then published, was applied to the elucidation of the structural dimensions of the permanganates of the alkalies. The new ratios were termed by him "topic axial ratios," from *τόπος* "space." The author adopted Muthmann's term for the sake of uniformity, in further communications on the subject, but time has only strengthened his original view that this is not a very fortunate appellation for the constants, and he has latterly felt constrained to revert to the term first applied, with the addition, as stated, of the word "molecular." "Molecular distance ratios" are the expression of the relative distances apart of the centres of gravity or other representative points, taken analogously, of the molecular structural units, along the three directions in space.

This idea of molecular distance ratios has proved a remarkably fruitful one, and appears likely to lead to great advances in the near future. It at once places the relative dimensions of the space-lattices of analogously constituted substances, such as those of the two series before us, on a mathematically sound basis. For they are dependent on three quantities only, each of which is capable of practical determination in the laboratory with the very highest degree of accuracy; these are namely, (1) the goniometrical crystal elements which now can be determined with an accuracy comparable with that of atomic weight determinations; (2) the specific gravity, whose determination is now possible with an accuracy vastly greater than was formerly the case, thanks to the admirable immersion method of Retgers and to improve-

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<sup>1</sup> *Zetscher fur Kryst.*, 1894, 22, 497.

ments made by the author in the pyknometer method, for use when the Retgers method is inapplicable on account of the density being superior to that of any immersion liquid; and (3) molecular weight, the sum of the atomic weights of the elements present, atomic weight determinations being notoriously the most accurate of all chemical analytical operations.

The mode of combining these quantities to produce the molecular distance ratios will be seen by quoting the formulæ applicable to the two series of isomorphous salts under discussion. The essence of the method is, first to decide on the nature of the space-lattice, from the goniometrical results, aided by the indications of cleavage directions, for these planes of maximum cohesion are those along which the points of the space-lattices are most densely strewn; we can thus arrive at the shape of the elementary parallelepipedon. We then derive its three dimensions in space for the various members of the series in such a manner that these three dimensions bear the same relation to each other as do the crystallographic axial ratios  $\alpha : b : c$ , while at the same time the volumes of the parallelepipeda for the various salts are related to each other as are the values of the molecular volume, the well-known constant obtained by dividing the molecular weight by the specific gravity. We thus arrive at the relative dimensions in space of the parallelepipeda of the various members of the series.

The molecular distance ratios are represented by the three Greek letters  $\chi$ ,  $\psi$ ,  $\omega$ , which refer as a rule to the three axial directions of the crystal  $a$ ,  $b$ ,  $c$ . The ratios are written, therefore, as  $\chi : \psi : \omega$ , analogous to the crystallographic axial ratios  $\alpha : b : c$ . In certain cases, one of which is a particular form of rhombic space-lattice, and another is that of a pseudo-hexagonal, although really rhombic, space-lattice, such as we have in the series of alkali sulphates and selenates before us, a fourth ratio

may be added,  $\xi$ , representing the separation of the molecular centres along the sides of the rhombic base, which is not in these cases a crystallographic axial direction. As the fourth distance can always be obtained from the other three, however, the number of essential distances is only three, and in the pseudo-hexagonal case of the simple sulphates and selenates the three essential ones only will be given, and labelled  $\chi$ ,  $\psi$ , and  $\omega$ . The letter  $\omega$ , as always, represents the distance separating the points along the vertical axis; but  $\psi$  represents the distance between points along the direction of the horizontal axis  $a$  (see Fig. 45), the direction usually represented by  $\chi$  in the ordinary space-lattice, while  $\chi$  represents two equal distances of separation of the molecular points, equally inclined at nearly  $60^\circ$  to the axis  $a$  on each side of the latter. If the pseudo-hexagonal were a truly hexagonal structure,  $\chi$  and  $\psi$  would be equal and  $\chi$  would represent both.

Perhaps it will be most satisfactory to give first the formulæ which express the molecular distance ratios in

the most general case, that of a triclinic crystal, the elementary parallelepipedon of the space-lattice of which is represented in Fig. 43, and then to show how they become simplified as symmetry is introduced and increased.

If the axial ratios are expressed as usual by  $a$ ,  $b$ ,  $c$ , where  $b=1$ , and the angles between the axes, which in this general case are all other than  $90^\circ$ , as  $\alpha$ ,  $\beta$ ,  $\gamma$ ; also if  $\theta$  represent

the dihedral angle between two of the faces (001) and (010); and if  $V$  represent the molecular volume, that is, molecular weight / specific gravity, then :

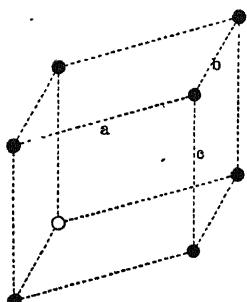


FIG. 43.—TRICLINIC  
SPACE-LATTICE.

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta \cdot \sin \gamma \cdot \sin \theta}}$$

$$\psi = \sqrt[3]{\frac{V}{ac \sin \beta \cdot \sin \gamma \cdot \sin \theta}}$$

$$\omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta \cdot \sin \gamma \cdot \sin \theta}}$$

In the case of a monoclinic crystal, such as one of the series of monoclinic double sulphates or selenates under consideration, the space-lattice is one the elementary

parallelepipedon of which is represented in Fig. 44. The crystallographic angles  $\alpha$  and  $\gamma$ , and the dihedral angle  $\theta$ , are now  $90^\circ$ , so that the only angle left in the formula is  $\beta$ , the monoclinic axial angle. Hence the formulæ simplify greatly, to the following :

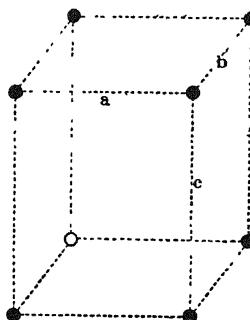


FIG. 44.—MONOCLINIC  
SPACE-LATTICE.

$$\chi = \sqrt[3]{\frac{a^2 V}{c \sin \beta}}, \quad \psi = \sqrt[3]{\frac{V}{ac \sin \beta}}$$

$$\omega = \sqrt[3]{\frac{c^2 V}{a \sin \beta}}$$

These are the formulæ which were actually used in calculating the molecular distance ratios of the salts of the series  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ .

When the symmetry rises still further to orthorhombic,  $\beta$  also becomes  $90^\circ$ , so that  $\sin \beta$  disappears, the formulæ thus becoming :

$$\chi = \sqrt[3]{\frac{a^2 V}{c}}, \quad \psi = \sqrt[3]{\frac{V}{ac}}, \quad \omega = \sqrt[3]{\frac{c^2 V}{a}}$$

These three last formulæ were given by the author in the 1894 memoir introducing molecular distance ratios, as being those applicable to the rhombic sulphates and selenates, and the molecular distance ratios for these salts were worked out from them.

If the symmetry rises still further to tetragonal,  $a=b=1$ , so that :

$$\chi = \psi = \sqrt[3]{\frac{V}{c}}, \text{ and } \omega = \sqrt[3]{c^2 V}.$$

When finally the full symmetry of the cubic system is reached, and  $a=b=c=1$ , then obviously :

$$\chi = \psi = \omega = \sqrt[3]{V}.$$

The formulæ for the space-lattices of the trigonal and hexagonal systems can readily be worked out on similar lines, and also in fact all those for the whole of the remainder of the fourteen Bravais space-lattices,<sup>1</sup> so that the method is a perfectly general one, applicable the moment we know the nature of the space-lattice present in the crystal structure.

With respect to the structure of the rhombic sulphates and selenates  $R_2\overset{S}{Se}O_4$ , the remarkably close simulation of hexagonal symmetry, which has been referred to in the last chapter, led the author in 1905 to work out the molecular distance ratios on the supposition of a pseudo-hexagonal space-lattice. It had been suggested by von Fedorow that the series did really possess such a structure, and it was interesting anyhow to see if distance ratios, worked out on the basis of such an assumption, afforded similar comparative results for the structural dimensions of the various members of the series to those derived in 1894 on the assumption of ordinary rhombic structural symmetry. The new ratios, however, did lead to precisely similar comparative results, but as the evidence seems to be so strong for such a structure, the author has definitely adopted it, and the mode of deriving the ratios will therefore be briefly described. Fig. 45 will render the process clear.

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<sup>1</sup> See the author's book "Crystallography and Practical Crystal Measurement" shortly to be published by Messrs. Macmillan & Co. Ltd.

It is assumed that there has been a slight deformation from hexagonal symmetry, and that a rhombus of  $60^\circ$  has been slightly flattened to one of which the angle, double the angle  $ap = (100):(110)$ , varies in the different salts of the series from  $58^\circ 4'$  to  $59^\circ 38'$ . The crystal is supposed to be rotated  $90^\circ$  about the vertical axis, so as to bring it into the position corresponding to the hexagonal prism of the first order. The hexagon in Fig. 45 is the plan of this hexagonal prism, and the six triangles into which the hexagonal axes divide it represent the corresponding pyramid. The former consists of two pairs of primary prism faces  $p$ , and the pair of brachypinakoid faces  $b$ . The pyramid is formed by the four primary pyramid faces  $o$ , and the pair of brachydome faces  $q'$ . The dots at the corners represent the points of the space-lattice point-system. The six rays of the star being parallel to the  $b$  and  $p$  faces, two to the former and four to the latter, it will be obvious that the obtuse angle of each rhombus is double of the angle  $bp$ , and the acute angle double of the angle  $ap$ .

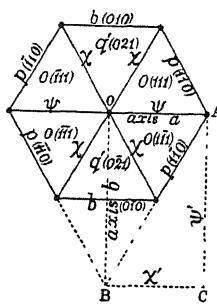


FIG. 45.  
PSEUDO-HEXAGONAL  
STRUCTURE

If  $\chi, \psi, \omega$  represent the new molecular distances, and  $\chi', \psi', \omega'$  those on the assumption of ordinary rhombic structural symmetry, then the direction  $OA$  of the rhombic axis  $a$  is that of the new intermediate molecular distance  $\psi$ , identical with the ordinary  $\chi'$ . The direction  $OB$  of the ordinary  $\psi'$ , corresponding to the rhombic axis  $b$ , is now no longer a molecular distance in the ordinary sense, being replaced by a pair of equal pseudo-hexagonal molecular distances  $\chi$  about  $30^\circ$  (varying from a minimum of  $29^\circ 2'$  in thallium selenate to a maximum of  $29^\circ 49'$  in potassium selenate) on each side of it, slightly different in length from  $\psi$ ; if, however, the length of this diagonal

(axis  $b$ ) of the rhombus is desired to be also calculated, it can readily be done, and is labelled  $\xi$ . The vertical axis of the crystal, the axis  $c$ , is identical in direction with both  $\omega$  and  $\omega'$ . If, as before,  $V$  represents the molecular volume, the values of the molecular distance ratios thus derived are as under:—

$$\chi = \frac{1}{2} \sqrt{1 + a^2} \cdot \sqrt[3]{\frac{2V}{ac}},$$

$$\psi = \sqrt[3]{\frac{2a^2V}{c}},$$

$$\omega = \sqrt[3]{\frac{2c^2V}{a}}.$$

These three formulæ were used to calculate the molecular distance ratios given in the next table, which records the results for the series  $R_2\overset{S}{Se}O_4$ .

The densities of the salts of both series were determined, in all those cases where the specific gravity was not higher than that of methylene iodide (3.342), by the suspension method, a mixture of benzene and methylene iodide being employed as the immersion liquid. The specific gravity of the denser salts was of necessity determined by the pyknometer method, which, however, had greatly ~~been~~ increased in accuracy by improvements ~~in~~ being ~~made~~ tightly pressed over the capillary of ~~the~~ <sup>the</sup> upper to ~~the~~ of arrest evaporation of the carbon tetrachlorid used as the auxiliary liquid, by means of a spring which forms part of the supporting brass wire stand in which the whole pyknometer fits, and which also serves as a means of handling the instrument without touching the pyknometer itself. As the result of a very thorough investigation, moreover, it was discovered that the highest result with the thus improved pyknometer method invariably corresponded with the mean value of the results derived from the immersion method, in all cases where

both methods were equally available and could be properly compared. Hence, by taking the highest result obtained from the pycnometer method in any case where this method was alone available, a result comparable with those obtained by the immersion method was arrived at.

### Space - dimensions of the Rhombic Series

$R_2^S SeO_4$ .—The next table presents the results for the rhombic series of simple salts. In the second column are

*Comparative Values of Structural Constants.*

Salt	Density at $20^\circ/4^\circ$ .	Molecular weight	Molecular volume.	Axial ratios			Molecular distance ratios		
				<i>a</i>	<i>b</i>	<i>c</i>	<i>x</i>	<i>y</i>	<i>ω</i>
$K_2SO_4$ . . .	2.666	173.04	64.91	0.5727	1.0	0.7418	3.8810	3.8574	4.9064
$Rb_2SO_4$ . . .	3.615	265.14	73.34	0.5728	1.0	0.7485	4.0304	4.0081	5.2360
$Cs_2SO_4$ . . .	4.246	359.14	84.58	0.5712	1.0	0.7531	4.2187	4.1849	5.5173
$Tl_2SO_4$ . . .	6.765	500.50	73.98	0.5555	1.0	0.7328	4.0320	3.9644	5.2299
$(NH_4)_2SO_4$ . . .	1.772	131.20	74.04	0.5635	1.0	0.7319	4.0712	4.0651	5.2020
$K_2SeO_4$ . . .	3.007	219.82	71.67	0.5731	1.0	0.7310	4.0291	4.0068	5.1171
$Rb_2SeO_4$ . . .	3.902	311.92	79.94	0.5708	1.0	0.7386	4.1672	4.1815	5.3461
$Cs_2SeO_4$ . . .	4.456	405.92	91.09	0.5700	1.0	0.7424	4.3457	4.3040	5.6058
$Tl_2SeO_4$ . . .	6.875	547.80	79.61	0.5551	1.0	0.7243	4.1124	4.0763	5.3189
$(NH_4)_2SeO_4$ . . .	2.194	177.98	81.12	Not comparable			4.5394	4.2963	5.1506 <sup>1</sup>

given the specific gravities for the uniform temperature of  $20^\circ$  C., compared with water at  $4^\circ$  taken as unity. Then follow the molecular weights employed in the calculations of the molecular volumes, which are given in the next column. Then come the crystallographic axial ratios, and, finally, the molecular distance ratios, calculated as explained on the assumption of a pseudo-hexagonal structure.

A study of this table, and of the next one showing the amounts of the changes for the various replacements, reveals the following important facts:—

<sup>1</sup> The molecular distances of monoclinic ammonium selenate were calculated on the assumption of a similar pseudo-hexagonal structure to that of the nine rhombic salts. Such a structure is strikingly evident as regards the prism zone, the angles of the prism faces being  $59^\circ 38'$  and  $30^\circ 0'$ , the prism zone thus resembling the well-known pseudo-hexagonal prism zone of the nine rhombic salts to a remarkable degree, considering the change of system.

(1) The replacement of potassium by rubidium, and this alkali metal in turn by cæsium, that is, an increase in the atomic weight of the alkali metal, is accompanied by an increase in the separation of the analogous points representing the molecular structural units along each of the directions of the pseudo-hexagonal axes, and, in general, along every direction in which points are shown

(2) The increase in the separation of contiguous units of the homogeneous crystal structure augments as the atomic weight rises, so that the intermediate values for the rubidium salt of either group are somewhat nearer to those for the potassium salt than to those for the cæsium salt.

(3) A similar extension of the molecular distances accompanies the replacement of sulphur by selenium.

It will be observed that the values for the pair of distances  $\chi$  and for  $\psi$  are very nearly equal; they would be all three identical if the crystal were truly, instead of only pseudo-, hexagonal.

(4) The amount of expansion as the atomic weight of the alkali metal increases is much greater along the vertical axis than along the lateral directions  $\chi$  and  $\psi$  in the crystal, and this greater expansion along the vertical axis, as one metal is replaced by another of higher atomic weight, appears relatively greater when considered in proportion to the original dimensions of the crystal structure along the directions compared.

*Changes in Molecular Distance Ratios.*

Replacement		$\chi$	$\psi$	$\omega$
K in $K_2SO_4$ by Rb	...	0.1494	0.1465	0.2402
Rb in $Rb_2SO_4$ by Cs	...	0.1883	0.1810	0.2809
K in $K_2SeO_4$ by Rb	...	0.1381	0.1247	0.2290
Rb in $Rb_2SeO_4$ by Cs	...	0.1785	0.1725	0.2597
S in $K_2SO_4$ by Se	...	0.1481	0.1494	0.1207
,, $Rb_2SO_4$ ,,	...	0.1368	0.1276	0.1095
,, $Cs_2SO_4$ ,,	...	0.1270	0.1191	0.0883

The table just given, in which the actual amounts of the changes are shown, all the changes being increases in the dimensions of the elementary parallelepipeda, will render this point quite clear. It is obvious that while the increases in the lateral dimensions (the two  $\chi$  directions and the third  $\psi$  direction) are nearly the same, the extension along the vertical axis is greater; and greater, moreover, than in the proportion of the original length along that axis compared with the original lengths along the lateral axes, this proportion being roughly 5 : 4 at the start, but 6 : 4 after the replacement by a heavier alkali metal. This practically and visually translated means that, while the crystal expands parallel to itself equatorially, it very perceptibly elongates vertically when one alkali metal is replaced by another of higher atomic weight.

Now the converse of this is true of the replacement of sulphur by selenium, for, in extension of the statement given in (3), we may now add :—

(5) When the sulphur in the sulphate of either potassium, rubidium, or cæsium is replaced by selenium, the extension of the crystal structure occurs to a markedly less extent along the vertical crystallographic axis than along the lateral directions, and this pre-eminence in equatorial expansion becomes even relatively greater if the relative original molecular distances are considered. The equatorial expansions along  $\chi$  and  $\psi$  are again not far from equal.

Conclusions (4) and (5) are of the utmost importance, for they amount to the proof, for the first time incontrovertibly advanced, that *specific atomic chemical replacements are accompanied by definitely localised structural changes, specific parts of the crystal structure being most largely affected*. The conclusion from this fact that *particular chemical atoms occupy definitely orientated positions in the chemical molecule, the crystallographic*

*structural unit in the solid state*, is both obvious and inevitable. It is one of far reaching importance.

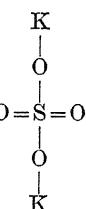
In the case before us it is clear that replacement of the alkali metal brings about changes of dimensions most pronounced along the vertical direction, while replacement of the sulphur by selenium affects predominatingly the equatorial directions. This would appear to indicate that the two atoms of the alkali metal, or their spheres of influence, are situated along the vertical axis, while the sulphur or selenium atom or its sphere of influence occupies the centre. Such a supposition is precisely that which is suggested by the probable symmetrical stereometric arrangement of the atoms in the chemical molecule of the type before us, which may be expressed, as far as this is possible in one plane, by the currently accepted graphic formula for potassium sulphate, which is given in the margin. As was stated by the author in 1906 in an article in *Science Progress*:<sup>1</sup>

“The actual arrangement in space is probably that of a structure consisting of three regular point-systems, with similar coincidence movements (Deckschreibungen), the first being of sulphur or selenium atoms, the second of four times as many oxygen atoms, and the third of twice as many alkali metallic atoms—the three systems interpenetrating in such a manner as to produce equilibrium, and being so mutually arranged that the sulphur or selenium system lies centrally with respect to the other two, and the metallic system in such wise as would affect chiefly the vertical direction. Barlow's type 57a would appear to fulfil these conditions.”

These conclusions are further strengthened by the directions of the changes in the crystal angles. Thus, when potassium is replaced by rubidium or caesium the primary angles  $cq = 001:011$  and  $co = 001:111$  both increase, corresponding to the elongation of the vertical axis; but when sulphur is replaced by selenium these angles diminish, corresponding to an equatorial bulging.

We must now consider the teaching of molecular distance

<sup>1</sup> *Some Recent Progress in Chemical and Structural Crystallography*, p. 20.



ratios with respect to the positions occupied in the series by the ammonium and thallium salts. Considering first the case of ammonium we observe :—

(6) The molecular distance ratios of ammonium sulphate are very close to those of rubidium sulphate, and, on the average, ammonium sulphate occupies a position, as regards its dimensions in space, just beyond that of rubidium sulphate and on the cæsium side.

Thus the replacement of potassium by ammonium is accompanied only by about the same amount of separation of the molecular centres as is observed when rubidium is substituted for potassium. This is a truly significant result, for it means that if the space-lattices are strictly comparable (and proofs will subsequently be adduced that they are), the two atoms of the alkali metal are replaced by ten atoms of the two radicle groups  $\text{NH}_4$ , without more distension of the structure than if merely two rubidium atoms had been introduced instead of two potassium atoms, and with very much less expansion of the structure than if two cæsium atoms had been substituted. It means that there is room in the original structure for the introduction of eight additional atoms of hydrogen, besides the two nitrogen atoms which may be assumed to compensate more or less for the removal of the two alkali metallic atoms. The author has felt unable, largely on account of this remarkable fact, to accept any theory of crystal structure in its entirety which is built on the idea of absolutely close packing of the atoms or their spheres of influence. This interesting subject will be reverted to again after considering the results of the volume investigation of the thallium salts and of the ammonium and thallium salts of the double salt series.

Next, in regard to thallium, we note the following facts from the results given in the table of molecular distance ratios.

(7) The molecular distance ratios of thallium sulphate

and selenate are almost identical with those of the rubidium salts, and also consequently with those of the ammonium salts (completely as regards the sulphate, and in the case of ammonium selenate so far as that ordinarily monoclinic salt is comparable).

Thus structurally thallium takes a place in the series not far removed from rubidium, in this respect resembling ammonium. This double fact leads us to another conclusion of prime significance, which may be formulated as follows :—

(8) *The law of progression of the crystal properties, morphological and structural, according to the atomic weights of the interchangeable elements, which states that the crystal properties are functions of those atomic weights, applies only to the strictly homologous isomorphous salts of which the interchangeable elements belong rigidly to the same exclusive family group of the periodic classification of the elements.* As thallium does not belong to the same family as potassium, rubidium, and cæsium, and ammonium must be excluded from the family for the obvious reason that it is not an element at all but a radicle group simulating one, the only elements to which the law applies are potassium, rubidium, and cæsium, which fulfil the conditions of strict family relationship absolutely.

The law of progression being inoperative in the cases of the ammonium and thallium salts, the structural dimensions, as well as the morphological angles, are merely adequately close to those for the potassium, rubidium, and cæsium salts to permit of their inclusion in the same isomorphous series, using this term in a wider sense which the author defines as follows :—

(9) *An “isomorphous series” is one the members of which bear some definite chemical analogy and crystallise according to the same system of symmetry and in the same class of that system, and develop the same forms*

inclined at angles which only differ by a very few degrees, rarely exceeding  $3^{\circ}$ .<sup>1</sup>

For a series in which the interchangeable elements are strictly members of the same family group, such as potassium, rubidium, and cæsium, the author has adopted a distinctive name, which was suggested by Linck,<sup>2</sup> namely "eutropic," from " $\epsilonὐτροπή$ " meaning "a regularly progressive change" (*regelmässige Änderung*). Hence:—

(10) *An "eutropic" series is one in which the small angular differences, and also the structural and physical<sup>3</sup>, properties of the crystals, obey the law of progression according to the atomic weight of the interchangeable elements which give rise to the series and belong to the same family group of the periodic classification.*

(11) *Thallium sulphate and selenate and ammonium sulphate belong to the orthorhombic isomorphous series  $R_2^S SeO_4$ , while the sulphates and selenates of potassium, rubidium, and cæsium belong not only to this same isomorphous series, but also to the still more exclusive eutropic series within it.*

The increase in the molecular distance ratios when potassium is replaced by rubidium or cæsium, or by thallium or the radicle ammonium, is largely due to the increase in molecular volume. The molecular volume of either rubidium sulphate or selenate is intermediate between the volumes of the potassium and cæsium salts of the same group, and the greater increase in volume occurs for the replacement of rubidium by cæsium. In the sulphate group the replacement of potassium by rubidium evokes an increase of 8.4 units of volume, and of 8.3 in

<sup>1</sup> The maximum difference met with in the rhombic series in question has been shown to be only  $1^{\circ} 21'$ , which occurs between thallium and potassium selenates in the case of one angle. The maximum difference yet met with in the monoclinic double sulphate and selenate series is  $2^{\circ} 21'$ .

<sup>2</sup> *Zeitschr. für Phys. Chem.*, 1896, 19, 197.

<sup>3</sup> This will be dealt with and fully proved in subsequent chapters.

the selenate group. The replacement of rubidium by caesium, however, calls forth an increase in volume of 11.4 and 11.35 units in the two respective groups. The molecular volumes of the ammonium and thallium salts are wonderfully near those of the rubidium salt of the same group, just as are the directional dimensions of the elementary parallelepipeda.

The replacement of sulphur by selenium in any of the sulphates is accompanied by an increase of volume which varies from 6.5 to 6.7 units, the minimum corresponding to the replacement in caesium sulphate, and the maximum to the interchange in potassium sulphate. Thus the effect of the substitution of selenium for sulphur diminishes as the weight of the initial molecule increases.

The changes in the molecular distance ratios—the dimensions of the elementary parallelepipeda and the distances of separation of the points (representing the molecules) of the space-lattice—are, in fact, the directional interpretation of the changes in molecular volume. We have shown conclusively that the molecular volumes of the potassium, rubidium, and caesium salts are strictly comparable with each other, inasmuch as the space-lattices of the crystals of those salts are undoubtedly constructed on the same plan, differences of dimensions (those indicated by the distance ratios and molecular volumes) alone occurring.

Before concluding this review of the structural results of the investigation of the simple sulphate and selenate series, however, it will be well to state the evidence for the comparability of the space-lattices of the ammonium and thallium salts with those of the salts of these alkali metals proper. For it is quite conceivable that the space-lattices may not be truly comparable with those of the eutropic series, and that instead of there being loose enough packing, involving interspaces, to admit of the introduction of the additional eight atoms of hydrogen of the ammonium

group without disturbing the existing arrangement more than would the introduction of rubidium atoms for potassium, a general expansion in some way of the whole molecule might occur, leaving the relative dimensions in space pretty much the same as they were. The evidence, however, is against such an explanation, and as this evidence forms one of the difficulties which the author experiences in accepting the theory of crystal structure based on the closest packing of the constituent atoms or their spheres of influence, it is advisable to give some account of it. The whole drift of the author's own work is against such a supposition of non-comparability, and the assumption is conclusively negatived by the interesting and important researches of Barker<sup>1</sup> on the regular growth of soluble salts on each other. Barker has shown that the perchlorates, like the permanganates investigated in 1894 by Muthmann,<sup>2</sup> of rubidium, ammonium, and thallium, possess almost identical molecular volumes and distance ratios, just like the analogous sulphates and selenates, and that they readily form parallel growths on each other; and he further conclusively proved from a whole series of experiments with a large number of salts that only such substances as possess similar molecular volumes and distance ratios exhibit the property of forming parallel growths. It is precisely the congruency, that is, the near equality of the absolute lengths of the sides of the elementary parallelepipeda of the space-lattices, and therefore the strict compatibility and comparability of the latter, that induces the formation of parallel growths of the one upon the other.

The author has also shown that rubidium and ammonium selenates crystallise together in large and very perfect rhombic crystals, which may contain more

<sup>1</sup> *Min. Mag.*, 1907, 14, 235; and *Journ. Chem. Soc.*, 1906, 89, 1120.

<sup>2</sup> *Zeitschr. fur Kryst.*, 1904, 22, 527.

than 60 per cent. of ammonium selenate, although the common form of that dimorphous salt is monoclinic. The fact is due to the nearness to identity of the structural dimensions of rubidium and ammonium salts, as indicated by the closeness of the molecular volumes and distance ratios, particularly in the cases of rhombic ammonium and rubidium sulphates. If rhombic crystals could be isolated of pure ammonium selenate, it is probable that their molecular volumes and distance ratios would be even closer to those of rubidium selenate than are the values for the monoclinic variety given in the table. Great difference of these constants is undoubtedly unfavourable to the formation of mixed crystals, while close approximation is highly favourable.

The latter conclusion has been confirmed by two other independent observers, Wulff and Gossner. Wulff<sup>1</sup> has shown that large and beautifully transparent homogeneous mixed crystals may be obtained of ammonium and rubidium sulphates, the molecular volumes of which only differ by 0·7, whereas other members of the sulphate group either do not form mixed crystals at all or, if so, not transparent and homogeneous ones; for instance, potassium and cæsium sulphates altogether decline to form mixed crystals, the difference of volume being at its maximum.

Gossner<sup>2</sup> has shown still more recently that mixed crystals are probably true homogeneous structures and not mere mechanical mixtures. Many of the measurements of Wulff had already indicated the likelihood of this. Gossner considers it now as a proved fact that only those members of isomorphous series form mixed crystals the molecular volumes of which are close together. He explains it on the assumption that the force of crystallisation brings about actual equalisation of the molecular volumes, one constituent contracting and the other expanding in the act

<sup>1</sup> *Zeitschr. für Kryst.*, 1906, **42**, 558.

<sup>2</sup> *Zeitschr. für Kryst.*, 1907, **43**, 130.

of crystallising together, the amount of change of volume being only of the same order as had been observed by the author (Tutton<sup>1</sup>) to occur in the thermal expansion of the sulphates of potassium, rubidium and caesium.

Whether the explanation of Gossner be the true one, or whether it is merely a question of mechanical congruency of structural dimensions, the molecular distance ratios, within certain very narrow limits, it is absolutely certain that closeness of molecular volume and congruency of molecular distance ratios are the conditions both for the formation of parallel growths and for the production of mixed crystals. That it is not a question of similarity of crystal angles will be clear from the results given in the last chapter.

Hence, all these facts, derived quite independently from the investigations of four different observers, unite in indicating that the molecular volumes and molecular distance ratios of the rubidium and ammonium salts of this series, and probably also of the thallium salts, are strictly comparable; for these salts form both mixed crystals and parallel growths, and in the case of the ammonium and rubidium salts with the greatest ease and on a large scale. Therefore, it may be taken as proved that the spacial dimensions of the structural units of these salts, the molecular unit-parallelepipeda of their space-lattices, are almost identical. Hence, the packing must have been at least sufficiently open to have admitted the extra eight atoms of the two ammonium groups  $\text{NH}_4$ , for it has been proved that no general expansion occurs during the act of admission, but that on the contrary the lattice-dimensions remain practically the same.

#### Space-dimensions of the Monoclinic Series

$\text{R}_2\text{M}\left(\frac{\text{S}}{\text{Se}}\text{O}_4\right)_2 \cdot 6\text{H}_2\text{O}$ .—The specific gravities, molecular volumes, and molecular distance ratios of the salts of

<sup>1</sup> *Phil Trans.*, A, 1899, 192, 455.

the zinc group, which we have chosen as an example of the eight groups of these salts, are given in the next three tables.

Thallium zinc selenate forms crystals which are always opaque, and untrustworthy for density determinations, but excellent crystals of thallium zinc sulphate were obtained.

		Sp gr. at 20°/4°			Sp gr. at 20°/4°
AmZn sulphate	...	1.932	AmZn selenate	...	2.261
KZn	...	2.246	KZn	..	2.558
RbZn	..	2.591	RbZn	..	2.868
CsZn	...	2.875	CsZn	..	3.121
TlZn	...	3.720			
	Molecular Volume	Diff from K salt		Molecular Volume	Diff from K salt
KZn sulphate	196.16	—	KZn selenate	208.80	—
RbZn	205.58	9.42	AmZn	217.73	8.93
AmZn	206.38	10.22	RbZn	218.35	9.55
TlZn	206.45	10.29	CsZn	230.77	21.97
CsZn	217.97	21.81			
	Salt			$\chi$	$\psi$
Potassium zinc sulphate	...	..	...	6.0462 : 8.1562 : 4.1141	
Rubidium „	„	..	..	6.1436 : 8.3326 : 4.1754	
Ammonium „	„	..	..	6.1648 : 8.3670 : 4.1810	
Thallium „	„	..	..	6.1787 : 8.3351 : 4.1759	
Cæsium „	„	..	..	6.2415 : 8.5808 : 4.2561	
Potassium zinc selenate	..	..	..	6.1812 : 8.2880 : 4.2045	
Rubidium „	„	..	..	6.2913 : 8.4662 : 4.2492	
Ammonium „	„	..	..	6.2742 : 8.4684 : 4.2681	
Cæsium „	„	..	..	6.3710 : 8.7106 : 4.3300	

The conclusions which can be drawn from these tables are remarkably like those derived from the simple salts, and may be summarised as follows:—

(1) An increase in volume occurs to the extent of  $9\frac{1}{2}$  units when potassium is replaced by rubidium and of  $12\frac{1}{2}$  units when the latter is in turn displaced by cæsium, the total change of volume on replacing potassium directly by cæsium being 22 units. Expansion occurs, therefore, with rise of atomic weight of the alkali metal, and it becomes proportionately greater as the atomic weight becomes higher.

We saw in the case of the simple salt series that the same replacements of potassium by rubidium and caesium called forth an expansion of volume equal respectively to about  $8\frac{1}{2}$  and  $11\frac{1}{2}$  units, the total change on replacing potassium directly by caesium being from  $19\frac{1}{2}$  to 20 units. Hence, the same replacements call forth somewhat greater changes of volume in the less symmetrical crystals of the monoclinic series, than in the more symmetrical ones of the rhombic series.

The molecular distance ratios  $\chi$ ,  $\psi$ ,  $\omega$ , represent respectively the relative distances apart of the centres of the structural units along the directions  $a$ ,  $b$ ,  $c$ , of the three crystallographic axes, the structure being that of the ordinary monoclinic space-lattice. The whole molecule  $R_2M(SeO_4)_2 \cdot 6H_2O$ , is regarded as the structural unit for this purpose, and the points of the space-lattice as representative points, one analogously taken from each such molecule. It is probable that a double salt of this description consists of a number of similar interpenetrating point systems, on similar lines to those suggested for the simple rhombic sulphates and selenates ; but the particular space-lattice is of lower symmetry, namely, monoclinic, doubtless owing to the less symmetrical nature of the stereometric configuration of the molecule.

The changes in the molecular distance ratios will be rendered clearer with the aid of the next table, in which the increments for the various replacements are given.

*Changes in Molecular Distance Ratios.*

Replacement		$\chi$	$\psi$	$\omega$
K by Rb in sulphate	...	0.0974	0.1764	0.0613
Rb by Cs	„	0.0979	0.2482	0.0807
K by Rb in selenate	...	0.1101	0.1782	0.0447
Rb by Cs	„	0.0797	0.2444	0.0808
S by Se in K-salt	...	0.1350	0.1318	0.0904
„ „ Rb „	...	0.1477	0.1336	0.0738
„ „ Cs „	...	0.1295	0.1298	0.0739
			K	$\Sigma$

The following facts now become obvious:—

(2) The replacement of potassium by rubidium or the latter by caesium is accompanied by an extension of the distance separating the representative points of the structural units in all three axial directions, the maximum change being along the direction of the symmetry axis *b*. The distance ratios for the rubidium salt of either sulphate or selenate group are thus intermediate between those for the corresponding potassium and caesium salts. Even when the relative original lengths of the axes are taken into consideration, the extension along the symmetry axis still relatively preponderates.

(3) The molecular volumes and distance ratios of the ammonium salt of either group are very nearly identical with those of the rubidium salt. Hence the change both in volume and in the lengths of the sides of the elementary parallelepipedon of the space-lattice, when potassium is replaced by ammonium, is almost the same as when potassium is replaced by rubidium, and very much less than when caesium is introduced instead of potassium.

The average amounts of the changes of molecular volume for the three replacements, in the zinc and magnesium groups which have been completed, are 9.5 units for the replacement of potassium by rubidium, 10.3 for its replacement by ammonium, and 22.2 for its replacement by caesium. The average position of the ammonium salt as regards molecular distance ratios is 0.0225 beyond the rubidium salt, on the caesium side.

It is thus a fact in the double salt series, as in the rhombic series, that the ammonium salt occupies a position, as regards both its total volume and its directional dimensions, very close to that of the corresponding rubidium salt of the same group. Precisely the same facts are shown by the magnesium group, for which the ammonium salts have also been investigated, as by the zinc group, and there can be no doubt that it is a law

applicable to the whole series. Thus the ammonium group not only simulates the chemical behaviour of the alkali metals, but can also pack itself into the same crystal assemblage without extending it more than when another heavier alkali metal is substituted. Consequently, the suggestion made in connection with the simple rhombic salts, that the packing must be open enough to permit of the extra eight atoms of the two ammonium groups  $\text{NH}_4$  (ten non-metallic atoms for two metallic ones) being introduced, applies equally to the double salt series.

(4) The position of thallium zinc sulphate in the series, as regards both molecular volume and molecular distance ratios, is also quite close to that of rubidium zinc sulphate, and consequently to that of the ammonium salt. The general position of the thallium double salts, as of the thallium single salts, thus appears to be close to the rubidium and ammonium salts.

(5) The determination of the molecular volume in the monoclinic double salt series is pre-eminently a function of the alkali metal  $R$ , change of the second metal  $M$  being usually accompanied by a relatively small change of volume. Thus, although the difference between the atomic weights of magnesium (24.18) and zinc (64.9) is nearly the same as that between either potassium (38.85) and rubidium (84.9) or the latter and cæsium (131.9), yet the amount of alteration produced by interchange of magnesium and zinc is generally less than one unit of volume, whereas the amounts produced by interchange of the alkali metals have been shown to be 9.5 units for the replacement of potassium by rubidium, and as many as 22.2 units for its substitution by cæsium. The predominating rôle of the alkali metal in determining the molecular structural dimensions, as defined by the molecular volume and distance ratios, is thus most striking and significant. It renders the results of the investigation of the double salts all the more important as confirmatory

indications of the crystallographic relations of the three alkali metals, and of ammonium and thallium, in their isomorphous salts. For these relations are as clear in the double salts as they are in the simple sulphates and selenates, the *M*-sulphates and selenates playing an altogether subsidiary rôle.

(6) The replacement of sulphur in the monoclinic double salts by selenium is accompanied by an average increase of volume of about 12 units, nearly twice as much (there being now two electro-negative atoms in the molecule) as in the simple rhombic salts for which the increase averages  $6\frac{1}{2}$  units; and also by an extension of the dimensions of the elementary parallelepipedon of the space-lattice along all three axial directions, the amounts being proportionately greater along the *a* and *c* directions, and relatively less along the symmetry axis *b*, compared with those which occur on the replacement of one alkali metal by another.

Thus, while the replacement of the alkali metal affects most largely the direction of the symmetry axis *b*, the replacement of sulphur by selenium affects chiefly the dimensions in the symmetry plane, and, considering the original relative dimensions, particularly the *a*-axial direction in that plane. Hence, in the double salt monoclinic series we have the same important fact revealing itself as in the case of the simple rhombic series, that orientated changes accompany specific chemical replacements, thus affording additional proof that particular atoms of the molecule occupy specific positions in the crystal structure. A further substantiation is afforded by the fact concerning the crystal angles, that the changes are of opposite sign when a lighter is replaced by a heavier positive element (metal), and when the negative element sulphur is replaced by the heavier selenium; for the two changes are doubtless respectively connected with the two different predominating directional extensions of the space-lattice.

## CHAPTER XII

### THE OPTICAL RELATIONSHIPS OF THE SIMPLE AND DOUBLE SULPHATES.

THE rhombic symmetry of the series  $R_2\frac{S}{Se}O_4$  determines that the optical ellipsoid is fixed as regards its orientation, its axes being identical in direction with the crystallographic axes. The lengths of the axes of the ellipsoid vary, however, being determined by the values of the refractive index afforded along those directions ; they are either directly proportional to the refractive indices or to their reciprocals, according as we consider as the ellipsoid the "indicatrix" of Fletcher, or the ordinary vibrational velocity ellipsoid of Fresnel, which is the polar reciprocal of the indicatrix. The optical indicatrix is so convenient an expression of the optical characters of a crystal that we shall largely confine our attention to it. For the facts brought out by the comparison of either ellipsoid for the various salts of both series are identical. Fletcher, in his original memoir,<sup>1</sup> expresses the nature of the indicatrix as follows :—

"The characters of a ray of plane-polarised homogeneous light transmitted within a (crystalline) medium are indicated by geometrical characters at a corresponding point on an ellipsoid ; the direction of the ray is that of a diameter intersecting perpendicularly the normal drawn to the ellipsoid at the corresponding point : the velocity is inversely proportional to the length of the normal intercepted by the ray ; the plane of polarisation is perpendicular to the normal."

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<sup>1</sup> *Min. Mag.*, 1891, 9, 278.

The first operation of the optical investigation of a crystal is to discover the orientation of the optical ellipsoid, and if the goniometrical investigation has proved rhombic symmetry, as in the case of the simple rhombic salts, it only remains to confirm the fact of the identity of its axes with the crystallographic axes by preparing section-plates perpendicular to each axis in turn, and examining them in convergent polarised light, when through one of the sections the two optic axes with their systems of biaxial rings and hyperbolic brushes will be seen symmetrical to the centre of the field, the optic axes being inclined at their apparent acute angle.

Through a second plate, marginal rings will most likely be seen, but the optic axes themselves will be probably invisible in air, being separated at their obtuse angle, which will most likely be too large for emergence in air ; but the axes will be visible when the section is immersed in oil or monobromonaphthalene. The latter is especially suitable as the immersion liquid on account of its very high refractive index, which causes even optic axes separated at very wide obtuse (corresponding to small acute) angles, to be still rendered visible. There is no occasion to cut the third section if these two have been correctly selected beforehand. This will really have been done, for knowing that the crystals are rhombic, we should as a matter of expediency begin by cutting a pair of  $60^{\circ}$ -prisms with the aid of the special apparatus of the cutting-and-grinding goniometer described in Chapter V, symmetrical respectively to two of the axial planes, and with the refracting edge parallel to a crystallographic axis in each case ; by means of these prisms all three refractive indices could be determined. The relations of the latter would at once tell us which axis was the direction of the first median line, the bisectrix of the acute optic axial angle, and which was the obtuse bisectrix or second median line. This information would enable us to

proceed to cut the proper section-plates, from which, by determinations of the apparent acute and obtuse angles of the optic axes in monobromonaphthalene we could calculate the true angle separating the optic axes within the crystal, with the aid of the well-known formula :

$$\tan V_a = \frac{\sin H_a}{\sin H_o},$$

where  $V_a$  is the half of the true angle,  $H_a$  is the semi-acute angle as observed in the immersion liquid, and  $H_o$  is the apparent semi-obtuse angle in the liquid.

The problem in the case of the rhombic salts is thus a very simple one, provided we can readily obtain an adequate number of section-plates and 60°-prisms cut symmetrically to the crystallographic axes. This the cutting-and-grinding goniometer has enabled the author to do with the greatest facility, as described in Chapter V, never less than three duplicates of any plate or prism being employed in order to eliminate all possible slight errors from any source whatsoever.

**Rotation of the Optical Ellipsoid in the Monoclinic Double-Salt Series.**—The problem in the case of the monoclinic salts was not quite so straightforward, as the symmetry of the monoclinic system only requires the optical ellipsoid to be fixed as regards one axis, the symmetry axis perpendicular to the unique systematic plane of symmetry. The ellipsoid is free to rotate about this axis, and as a matter of fact the first striking result obtained as regards the monoclinic double salt series was the establishment of the fact that when one alkali metal is substituted for another the ellipsoid actually does rotate about the symmetry axis, and to a progressive extent following the order of the atomic weights of the alkali metals. We shall, therefore, begin the presentation of the optical results by exhibiting a table showing the orientation of the indicatrix in the various salts of our typical zinc group of the double salts. The

situation of one axis, say  $a$ , that for which the minimum refractive index  $\alpha$  is afforded, will be adequate to define the position of the ellipsoid, as  $\beta$  is identical in direction with the fixed symmetry axis of rotation.

*Inclination of Axis  $a$  of Indicative to Vertical Crystal-Axis  $c$*

AmZn sulphate	6 59	in front of $c$	AmZn selenate	3 24	in front of $c$
KZn	10 18	„ „	KZn	9 9	„ „
RbZn	16 43	„ „	RbZn	13 13	„ „
CsZn	30 16	„ „	CsZn	21 57	„ „

The 2nd M L of TlZn sulphate is  $13^{\circ} 20'$  behind  $c$ , but corresponds to  $\gamma$ , the salt being negative

The results given in the table are also graphically illustrated in Figs. 46 and 47. The dotted lines are the normals to the faces (100) and (001), the section of the

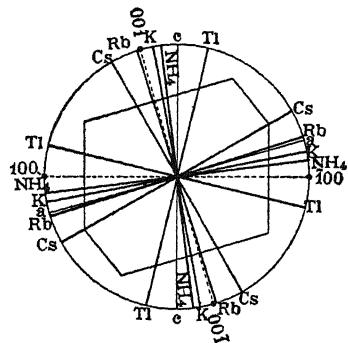


FIG. 46.—Zn Sulphate Group.

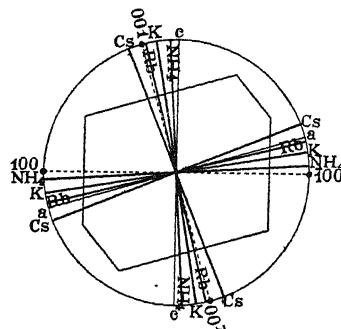


FIG. 47.—Zn Selenate Group.

POSITIONS OF MEDIAN LINES.

crystal by the symmetry plane, the plane of the paper, being also drawn. The crystallographic axes  $a$  and  $c$  are drawn in thin continuous lines, and the first and second median lines for the five salts in each case are drawn in thicker lines, the bunch of first median lines being those in the neighbourhood of the axis  $a$ , and the second median lines those about the vertical axis  $c$ . The facts which are evident are as follows:—

(1) The optical ellipsoid rotates about the symmetry axis when the atomic weight of the alkali metal is changed, the amount of rotation increasing with the atomic weight. The amount of rotation when rubidium is replaced by cæsium is twice as great as that which accompanies the replacement of potassium by rubidium, both rotations occurring in the same direction, forwards, away from the vertical axis, of the crystal.

(2) The position of the optical ellipsoid for the ammonium salt of each group is such that the second median line, the minimum axis  $a$  of the indicatrix or maximum axis of the Fresnel ellipsoid, lies very close to the vertical axis  $c$  of the crystal and on the left side of it. Thus when potassium is replaced by ammonium the ellipsoid rotates in the opposite direction to that in which it revolves when rubidium or cæsium is substituted, namely, backwards towards the axis  $c$ .

(3) When thallium is substituted for potassium the ellipsoid also rotates backwards, and so considerably as to bring the second median line well behind the vertical axis.

In the case of thallium zinc selenate the amount was undeterminable, as this salt develops a common property of the thallium double salts, that of opacity, to the extreme. Thallium zinc sulphate develops it least, and transparent crystals were obtained eventually for the optical work, affording perfectly trustworthy results.

#### General Optical Characters of the Two Series.

—The general optical characters of the various members of the monoclinic double salt series, whether sulphates or selenates, and whatever be the  $M$ -metal forming the group-subdivision, are extraordinarily even and similar, affording excellent comparisons of all the optical constants, not only the refractive index and all the constants derived from it, but also as regards the optic axial angles. The only extraordinary feature is the remarkable rotation of

the optical ellipsoid which has just been referred to, which of course carries with it the rotation of the directions for which the constants are compared, as regards such as lie in the symmetry plane. The symmetry axis at right angles to this plane, is, however, of course, fixed in direction. Hence it may be said that the constants show dispersion in the symmetry plane, but refer to one and the same direction when those for that axis of the ellipsoid are considered which is identical in direction with the symmetry axis. The outstanding remarkable fact is, however, that all observed dispersions of the optical constants in the symmetry plane, for the respective analogous potassium, rubidium, and cæsium salts, invariably exhibit the same order of progression as the atomic weights of those alkali metals, the function of the atomic weight being in general an increasing one.

While on one hand the monoclinic double salt series thus exhibits a remarkable similarity of optical characters throughout the whole series, on the other the simple rhombic salt series develops the greatest diversity of optical character, and yet exhibits all the same the still more extraordinary subservience to the law of progression according to atomic weight of the alkali metal. The potassium and cæsium salts have opposite characters, and the rubidium salts fall somewhere intermediate in optical character, and the progression according to the atomic weight of the alkali metal, in the dimensions of the optical ellipsoid, has been definitely proved to be the cause of the diversity. Still more permutations of optical character are introduced with the advent of ammonium and thallium, but no regular law governing them is now apparent. Thallium and ammonium sulphates resemble rubidium sulphate, but thallium selenate is more like cæsium selenate. A general survey of the optical characters is taken in the next table, which will render this diversity clearer. The old English letters in the last column refer to the axes of

the Fresnel ellipsoid,  $\alpha$  corresponding to  $\alpha$  of the indicatrix,  $\beta$  to  $\beta$ , and  $\gamma$  to  $\gamma$ .

Table of Optical Characters of Rhombic Series.

Salt	Plane of optic axes	Direction of first median line	Sign of double refraction	Optical scheme
$K_2SO_4$ . . .	$\alpha = (100)$	axis $c$	+	$b \alpha c$ +
$Rb_2SO_4$ (at $50^\circ$ — $180^\circ$ ) .	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$(NH_4)_2SO_4$	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$Tl_2SO_4$	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$Cs_2SO_4$ .	$b = (010)$	,, $c$	-	$c b \underline{\alpha}$
$K_2SeO_4$ .	$\alpha = (100)$	,, $c$	+	$b \alpha c$ +
$Rb_2SeO_4$ ..	$\alpha = (100)$	,, $c$	+	$b \alpha c$ +
$Tl_2SeO_4$ . . .	$c = (001)$	,, $b$	-	$c \underline{\alpha} b$
$Cs_2SeO_4$ . . . ..	$c = (001)$	,, $b$	-	$c \underline{\alpha} b$

**Refractive Indices of the Two Series.**—The optical constant of paramount importance, which governs practically all the rest, being the reciprocal measure of the velocity of light vibration in the crystals, is the refractive index, and it will be well to present the results of its determination for both series, at once. The refractive indices of the ten rhombic simple salts are all compared in the next table.

The following facts are at once apparent from this table of refractive indices:—

(1) The refractive indices of rubidium sulphate or selenate are intermediate between those of the corresponding potassium and caesium salts. An increase of refraction is observed to accompany an increase in the atomic weight of the alkali metal, and the increase becomes relatively greater as the atomic weight rises, than in mere simple proportion to that rise.

the optical ellipsoid which has just been referred to, which of course carries with it the rotation of the directions for which the constants are compared, as regards such as lie in the symmetry plane. The symmetry axis at right angles to this plane, is, however, of course, fixed in direction. Hence it may be said that the constants show dispersion in the symmetry plane, but refer to one and the same direction when those for that axis of the ellipsoid are considered which is identical in direction with the symmetry axis. The outstanding remarkable fact is, however, that all observed dispersions of the optical constants in the symmetry plane, for the respective analogous potassium, rubidium, and cæsium salts, invariably exhibit the same order of progression as the atomic weights of those alkali metals, the function of the atomic weight being in general an increasing one.

While on one hand the monoclinic double salt series thus exhibits a remarkable similarity of optical characters throughout the whole series, on the other the simple rhombic salt series develops the greatest diversity of optical character, and yet exhibits all the same the still more extraordinary subservience to the law of progression according to atomic weight of the alkali metal. The potassium and cæsium salts have opposite characters, and the rubidium salts fall somewhere intermediate in optical character, and the progression according to the atomic weight of the alkali metal, in the dimensions of the optical ellipsoid, has been definitely proved to be the cause of the diversity. Still more permutations of optical character are introduced with the advent of ammonium and thallium, but no regular law governing them is now apparent. Thallium and ammonium sulphates resemble rubidium sulphate, but thallium selenate is more like cæsium selenate. A general survey of the optical characters is taken in the next table, which will render this diversity clearer. The old English letters in the last column refer to the axes of

the Fresnel ellipsoid,  $\alpha$  corresponding to  $\alpha$  of the indicatrix,  $\beta$  to  $\beta$ , and  $\gamma$  to  $\gamma$ .

*Table of Optical Characters of Rhombic Series.*

Salt	Plane of optic axes	Direction of first median line	Sign of double refraction	Optical scheme
$\text{K}_2\text{SO}_4$ . . .	$\alpha = (100)$	axis $c$	+	$b \alpha c$ +
$\text{Rb}_2\text{SO}_4$ (at $50^\circ$ — $180^\circ$ ) .	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$(\text{NH}_4)_2\text{SO}_4$ . . .	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$\text{Tl}_2\text{SO}_4$	$b = (010)$	,, $\alpha$	+	$c b \alpha$ +
$\text{Cs}_2\text{SO}_4$ ..	$b = (010)$	,, $c$	-	$c b \underline{\alpha}$
$\text{K}_2\text{SeO}_4$ . . .	$\alpha = (100)$	,, $c$	+	$b \alpha c$ +
$\text{Rb}_2\text{SeO}_4$ ..	$\alpha = (100)$	,, $c$	+	$b \alpha c$ +
$\text{Tl}_2\text{SeO}_4$ .	$c = (001)$	,, $b$	-	$c \underline{\alpha} b$
$\text{Cs}_2\text{SeO}_4$ . . .	$c = (001)$	,, $b$	-	$c \underline{\alpha} b$

**Refractive Indices of the Two Series.**—The optical constant of paramount importance, which governs practically all the rest, being the reciprocal measure of the velocity of light vibration in the crystals, is the refractive index, and it will be well to present the results of its determination for both series, at once. The refractive indices of the ten rhombic simple salts are all compared in the next table.

The following facts are at once apparent from this table of refractive indices:—

(1) The refractive indices of rubidium sulphate or selenate are intermediate between those of the corresponding potassium and caesium salts. An increase of refraction is observed to accompany an increase in the atomic weight of the alkali metal, and the increase becomes relatively greater as the atomic weight rises, than in mere simple proportion to that rise.

RHOMBIC SERIES OF SIMPLE SALTS.

Comparative Table of Refractive Indices.

Crystal axis.	Light.	$K_2SO_4$	$Rb_2SO_4$	$Am_2SO_4$	$Cs_2SO_4$	$Tl_2SO_4$	$K_2SeO_4$	$Rb_2SeO_4$	$Am_2SeO_4$	$Cs_2SeO_4$	$Tl_2SeO_4$
$\alpha$	Li..	1.4924	1.5120	1.5297	1.5633	1.8739	1.5357	1.5504	1.5796*	1.5964	1.9476
	C..	1.4928	1.5124	1.5302	1.5657	1.8755	1.5362	1.5509	1.5806*	1.5969	1.9500
	Na..	1.4947	1.5144	1.5330	1.5662	1.8853	1.5380	1.5537	1.5846*	1.6003	1.9640
	Tl..	1.4956	1.5166	1.5359	1.5690	1.8964	1.5421	1.5570	1.5885*	1.6038	1.9782
	F..	1.4995	1.5194	1.5394	1.5725	1.9126	1.5646	1.5699	1.5935*	1.6084	1.9987
	G..	1.5024	1.5235	1.5445	1.5775	—	1.5517	1.5668	1.6005*	1.6152	—
$b$	Li..	1.4912	1.5108	1.5199	1.5615	1.8563	1.5320	1.5482	1.5561	1.5950	1.9331
	C..	1.4916	1.5112	1.5204	1.5619	1.8579	1.5325	1.5487	1.5571	1.5955	1.9355
	Na..	1.4935	1.5131	1.5230	1.5644	1.8671	1.5352	1.5515	1.5697	1.5989	1.9493
	Tl..	1.4935	1.5133	1.5238	1.5652	1.8778	1.5383	1.5547	1.5641	1.6024	1.9635
	F..	1.4982	1.5181	1.5291	1.5706	1.8935	1.5421	1.5586	1.5687	1.6070	1.9840
	G..	1.5012	1.5222	1.5340	1.5756	—	1.5478	1.5646	1.5752	1.6138	—
$c$	Li..	1.4950	1.5109	1.5177	1.5569	1.8493	1.5413	1.5549	1.5584*	1.5960	1.9426
	C..	1.4954	1.5113	1.5182	1.5573	1.8509	1.5418	1.5554	1.5594*	1.5965	1.9450
	Na..	1.4973	1.5153	1.5209	1.5598	1.8600	1.5446	1.5682	1.6630*	1.5939	1.9592
	Tl..	1.4994	1.5156	1.5237	1.5624	1.8704	1.5478	1.5615	1.6633*	1.6034	1.9737
	F..	1.5023	1.5183	1.5270	1.5660	1.8859	1.5518	1.5655	1.5713*	1.6080	1.9942
	G..	1.5052	1.5224	1.5318	1.5705	—	1.5576	1.5715	1.5781*	1.6148	—

Mean Refractive Indices of Rhombic Series.

$K_2SO_4$ ..	1.4952	0.0444	$K_2SeO_4$ ..	..	1.5306
$Rb_2SO_4$ ..	1.5136	0.0409	$Rb_2SeO_4$ ..	..	1.5645
$(NH_4)_2SO_4$ ..	1.5256	0.0438	$(NH_4)_2SeO_4$ ..	..	1.5694
$Cs_2SO_4$ ..	1.5635	0.0362	$Cs_2SeO_4$ ..	..	1.5997
$Tl_2SO_4$ ..	1.8708	0.0867	$Tl_2SeO_4$ ..	..	3578

\* The directions corresponding to the  $\gamma$  and  $\beta$  indices of monoclinic ammonium selenite are nearly but not quite those of the rhombic axes  $a$  and  $c$ , the directions of the axes  $b$  of the two systems correspond exactly, so that the  $\alpha$  indices are strictly comparable.

(2) The replacement of sulphur by selenium is also accompanied by an increase of refractive index, and such increase diminishes as the weight of the initial molecule increases.

These facts, and those which follow, will be rendered more obvious by the table of mean refractive indices which succeeds the main table. These values are obtained by taking the mean of  $\alpha$ ,  $\beta$ , and  $\gamma$  for sodium light, and they not only afford a concise expression of the comparative refraction of the crystals of the nine rhombic salts, but legitimately do so also in the case of the monoclinic selenate of ammonium, as the directional differences due to its different symmetry are eliminated in the process of averaging.

(3) The ammonium salts occupy a position as regards refraction near to the rubidium salts, and on the cæsium side.

(4) The thallium salts show extraordinarily high refractions compared with the potassium, rubidium, cæsium, and ammonium salts. This appears to indicate that optically the thallium salts are essentially different from all the other salts of the series.

The above conclusions remain equally valid when the refractive indices for higher temperatures up to 100° C. are compared. They have all been determined at such higher temperatures, and an universal reduction in refractive power found to accompany rise of temperature. The above facts, however, remain equally true throughout.

It is somewhat remarkable, although only in keeping with other known extraordinary optical properties of the thallium compounds in general, that while the morphological constants have been found to be so closely analogous to those of the corresponding rubidium and ammonium salts, the optical constants of the thallium salts soar far away, so that we are compelled to conclude that there is some fundamental difference, probably connected with

the different nature of the thallium atoms, between the salts of this metal and those of the alkali metals proper and of ammonium.

We will now compare the refractive indices of the monoclinic double salts of the typical zinc group. They are set out in the next table, which is followed by a shorter one showing the mean refractive index of each salt.

MONOCLINIC SERIES  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ . ZINC GROUP

*Comparative Table of Refractive Indices.*

Index	Name of light	KZn sulphate	RbZn sulphate	AmZn sulphate	CsZn sulphate	TlZn sulphate	KZn selenate	RbZn selenate	AmZn selenate	CsZn selenate
$\alpha$	Li	1.4748	1.4807	1.4858	1.4994	1.5880	1.5087	1.5129	1.5201	1.5290
	C	1.4752	1.4811	1.4862	1.4998	1.5887	1.5092	1.5134	1.5206	1.5295
	Na	1.4775	1.4833	1.4888	1.5022	1.5931	1.5121	1.5162	1.5240	1.5326
	Tl	1.4797	1.4857	1.4914	1.5047	1.5978	1.5151	1.5194	1.5273	1.5358
	F	1.4826	1.4886	1.4947	1.5079	1.6033	1.5189	1.5233	1.5316	1.5399
	G	1.4866	1.4929	1.4992	1.5125	1.6121	1.5244	1.5288	1.5381	1.5459
$\beta$	Li	1.4805	1.4856	1.4900	1.5020	1.6038	1.5146	1.5188	1.5260	1.5326
	C	1.4809	1.4860	1.4904	1.5024	1.6046	1.5151	1.5193	1.5265	1.5331
	Na	1.4833	1.4884	1.4930	1.5048	1.6093	1.5181	1.5222	1.5300	1.5362
	Tl	1.4857	1.4908	1.4957	1.5073	1.6143	1.5212	1.5253	1.5334	1.5394
	F	1.4889	1.4938	1.4990	1.5104	1.6203	1.5252	1.5293	1.5378	1.5435
	G	1.4929	1.4980	1.5036	1.5151	1.6295	1.5307	1.5351	1.5443	1.5495
$\gamma$	Li	1.4938	1.4947	1.4963	1.5064	1.6111	1.5297	1.5294	1.5344	1.5375
	C	1.4942	1.4951	1.4967	1.5068	1.6119	1.5302	1.5299	1.5349	1.5380
	Na	1.4969	1.4975	1.4994	1.5093	1.6163	1.5335	1.5331	1.5385	1.5412
	Tl	1.4994	1.5001	1.5021	1.5119	1.6219	1.5369	1.5365	1.5420	1.5446
	F	1.5027	1.5033	1.5056	1.5152	1.6281	1.5410	1.5405	1.5463	1.5488
	G	1.5067	1.5078	1.5102	1.5199	1.6377	1.5471	1.5466	1.5529	1.5549

*Mean Refractive Indices of Zinc Group.*

$1/3 (\alpha + \beta + \gamma)$  for *Na*-Light.

KZn-sulphate	..	..	1.4859	KZn-selenate	..	..	1.5212
RbZn-,,	..	..	1.4897	RbZn-,,	..	..	1.5238
AmZn-,,	..	..	1.4937	AmZn-,,	..	..	1.5308
CsZn-,,	..	..	1.5054	CsZn-,,	..	..	1.5367
TlZn-,,	..	..	1.6064				

The conclusions to be derived from these tables and similar ones for the other groups are precisely analogous to those derived from the tables of refractive indices of

the simple salts. They may be briefly summarised as under:—

(1) The refractive indices of any rubidium salt of the series  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$  are, without exception, intermediate between those of the potassium and caesium salts containing the same second metal and acid, and nearer to the values for the potassium salt. Hence, an increase in the atomic weight of the alkali metal is accompanied by an increase of the refractive power of the crystal, and the increase becomes relatively greater as the atomic weight rises.

(2) The replacement of sulphur by selenium is accompanied by an increase of refractive power.

(3) No relation can be traced between the atomic weight of the *M*-metal and the refractive indices.

(4) The whole of the refractive indices of the ammonium salts lie between those of the analogous rubidium and caesium salts.

In the two groups which have so far been completed, the magnesium and zinc groups, the values for the ammonium salt are generally nearer to the rubidium salt, but the separation from the latter increases as the weight of the molecule increases, until in the zinc selenate group the values are nearer to those of the caesium salt.

(5) The thallium double salts, as typified by thallium zinc sulphate, resemble the simple thallium salts in exhibiting exceptionally high refraction.

**Comparison of the Double Refraction.**—The values of the double refraction as measured by the difference between  $\alpha$  and  $\gamma$  for sodium light, a convenient ray of medium wave-length for the purpose of the comparison, are given in the next table.

We observe that: (1) Throughout both the simple and the double salt series the replacement of one alkali metal

by another of higher atomic weight is accompanied by a diminution of positive double refraction.

*Comparison of the Double Refraction  $N\alpha - \gamma - a$ .*

Salt	Sign	Value	Salt.	Sign	Value.
$K_2SO_4$	+	0.0038	$K_2SeO_4$	+	0.0094
$Rb_2SO_4$	+	0.0013	$Rb_2SeO_4$	+	0.0067
$Cs_2SO_4$	-	0.0064	$Cs_2SeO_4$	-	0.0014
$(NH_4)_2SO_4$	+	0.0121	$(NH_4)_2SeO_4$	+	0.0239
$Tl_2SO_4$	+	0.0253	$Tl_2SeO_4$	-	0.0147
KZn sulphate	+	0.0194	KZn selenate	+	0.0214
RbZn ,	+	0.0142	RbZn ,	+	0.0169
CsZn ,	+	0.0071	CsZn ,	+	0.0086
AmZn ,	+	0.0106	AmZn ,	+	0.0145
TlZn ,	-	0.0237			

(2) In the double salt series this merely results in the caesium salt exhibiting extremely low double refraction, still of positive sign; so very extremely low  $\beta$  values become in the magnesium sulphate and selenate groups that two of the three indices of refraction ( $\beta$  and one of the extreme indices) of the caesium salt become identical at the ordinary temperature for a wave-length in the blue, giving rise to the phenomenon of crossing of the optic axial planes.

(3) In the simple salt series, the amount of double refraction, being already very low in the case of the initial potassium salt, becomes reduced nearly to zero when the rubidium salt is reached, so that the continued operation of the rule established in (1) results in the sign of the double refraction being reversed when the caesium salt is reached. The interesting positions of approximate single refraction in the sulphate and selenate groups are found in the rubidium and the caesium salt respectively, the former showing the very small positive double refraction of only 0.0013, and the latter the similarly small negative double refraction of 0.0014. Moreover, in both cases the  $\beta$  index becomes identical with one of the extreme indices when the temperature is somewhat raised, giving rise to the crossing of the optic axial planes.

(4) Rubidium sulphate and cæsium selenate, in consequence of result (3), exhibit extraordinary sensitiveness of their optical characters to change of temperature and of the illuminating light, involving the display of the phenomenon of crossed-axial plane dispersion, absolute single refraction being exhibited at particular temperatures and with light of specific wave-lengths.

(5) In the double salt series, this latter interesting critical position of simulated single refraction is also arrived at for certain particular wave-lengths, in the cases of cæsium magnesium sulphate and selenate, and at the ordinary temperature.

The three refractive indices can never be absolutely identical at the same temperature and for the same wavelength (if they did, cubic symmetry would be optically simulated), but they become identical in pairs, simulating uniaxial optical characters; for the index which was formerly the intermediate one  $\beta$  does not necessarily become also identical with the two extremes  $\alpha$  and  $\gamma$  when the latter become identical owing to their convergence according to (1).

This interesting display of crossed-axial-plane dispersion, in consequence of the remarkable law governing the double refraction, will be dealt with more fully in the next chapter, as it has led the author to investigate the whole subject of crossed-axial plane dispersion, and to arrive at a general explanation of the phenomenon.

(6) The position of the ammonium salts as regards double refraction in the double salt series is intermediate between the rubidium and cæsium salts. In the simple salt series no rule can be traced on account of the complication introduced by the reversal of the sign, owing to the operation of the law stated in (1).

(7) The thallium salts again assert their optical singularity by displaying a larger amount of double refraction than the other double salts, and of opposite (negative) sign.

**Molecular Optical Constants.**—It has been fully proved in the last chapter that the molecular structural units of the crystals of the salts of each of the two isomorphous series in question, the elementary parallel-epipeda of the space-lattice in each case, are strictly analogous and comparable. Hence, it is interesting to compare the molecular refractive powers and molecular dispersions of the crystals of the various salts of the two series. For these also will be strictly comparable quantities, just as much so, indeed, as the molecular volumes themselves. These constants are compared therefore in the following tables, the calculations having been made with the aid of the well-known formulæ, both of Lorenz and of Gladstone and Dale, in which  $M$  signifies molecular weight,  $d$  specific gravity at  $20^\circ$  C compared with water at  $4^\circ$ , and  $n$  is refractive index.

RHOMBIC SERIES  $R_{Se}^S O_4$

*Molecular Refraction for Ray C.*

Formula used	Lorenz, $\frac{n^2-1}{n^2+2} \frac{M}{d}$			Gladstone, $\frac{n-1}{d} M$			Mean
	<i>a</i>	<i>b</i>	<i>c.</i>	<i>a</i>	<i>b.</i>	<i>c.</i>	
Crystal axis							
$K_2SO_4$ ..	18.87	18.83	18.95	32.01	31.94	32.18	32.04
$Rb_2SO_4$ ..	22.04	21.99	22.00	37.61	37.52	37.53	37.55
$(NH_4)_2SO_4$ ..	22.89	22.54	22.46	39.29	38.56	38.40	38.75
$Cs_2SO_4$ ..	27.51	27.44	27.26	47.71	47.56	47.17	47.48
$Tl_2SO_4$ ..	33.76	33.27	33.08	64.74	63.47	62.95	63.72
$K_2SeO_4$ ..	22.37	22.24	22.56	38.46	38.19	38.86	38.50
$Rb_2SeO_4$ ..	25.52	25.43	25.71	44.00	43.82	44.36	44.06
$(NH_4)_2SeO_4$ ..	—	26.13	—	—	45.22	—	45.92
$Cs_2SeO_4$ ..	31.05	30.99	31.03	54.41	54.28	54.37	54.35
$Tl_2SeO_4$ ..	38.45	38.05	38.31	75.63	74.47	75.23	75.11

The mean constants in the last column are obtained in each case by taking the mean of all three values corresponding to the three axial directions *a*, *b*, *c*, of the crystal, calculated by Gladstone's formula; and this column thus affords the best comparison of all.

MONOCLINIC SERIES  $R_2M(SeO_4)_2 \cdot 6H_2O$ .

Table of Molecular Refractions and Dispersions (Lorenz)

Salt	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = m$						Mol dispersion $m_e - m_\infty$		
	For ray C(H $\alpha$ )			For ray (H $\gamma$ ) near G					
	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
KZn sulphate	55.25	55.81	57.12	56.37	57.00	58.35	1.12	1.19	1.23
RbZn	58.51	59.02	59.96	59.73	60.26	61.26	1.22	1.24	1.30
AmZn	59.27	59.71	60.36	60.62	61.07	61.74	1.35	1.36	1.38
CsZn	64.09	64.37	64.85	65.46	65.74	66.25	1.37	1.37	1.40
TlZn	69.54	71.07	71.75	71.77	73.40	74.17	2.23	2.33	2.42
KZn selenate	62.37	62.98	64.52	63.93	64.57	66.23	1.56	1.59	1.71
RbZn	65.67	66.30	67.14	67.32	67.99	69.20	1.65	1.69	1.76
AmZn	66.26	66.88	67.77	68.11	68.76	69.66	1.85	1.88	1.89
CsZn	71.23	71.63	72.18	73.06	73.46	74.06	1.83	1.83	1.88

Molecular Refractions (Gladstone and Dale),  $\frac{n^2-1}{d} M$ , for Ray C.

	$\alpha$	$\beta$	$\gamma$
Potassium zinc sulphate	...	...	93.21
Rubidium	98.91	99.91	101.78
Ammonium	100.34	101.21	102.51
Cæsium	108.94	109.51	110.47
Thallium	121.53	124.82	126.33
Potassium zinc selenate	106.32	107.55	110.71
Rubidium	112.10	113.39	115.70
Ammonium	113.35	114.63	116.46
Cæsium	122.19	123.02	124.15

Mean Molecular Refractions,  $1/3(\alpha + \beta + \gamma)$  for Ray C.

KZn sulphate	...	...	94.83	KZn selenate	..	...	108.19
RbZn	...	...	100.20	RbZn	..	...	113.73
AmZn	...	...	101.35	AmZn	..	...	114.81
CsZn	...	...	109.64	CsZn	..	...	123.12
TlZn	...	...	124.23				

The following important facts are to be derived from the first table concerning the simple rhombic salts.

(1) The whole of the molecular optical constants of rubidium sulphate and selenate are intermediate in value between those for the corresponding potassium and cæsium

salts. The molecular refraction and dispersion increase with the atomic weight of the contained metal, such increase becoming greater as the atomic weight rises, the differences between the constants for the rubidium and caesium salts being greater than those between the values for the potassium and rubidium salts. This rule is equally valid whether the constants are calculated by the formulæ of Lorenz or of Gladstone and Dale, and whatever may be the wave-length for which the comparison is instituted. Moreover, as both density and refractive power have been proved to diminish on raising the temperature, these conclusions are independent of the temperature.

(2) The molecular refractions of the ammonium salts are very close to, and slightly higher than, those of the corresponding rubidium salt. The fact that ammonium selenate crystallises usually differently, in the monoclinic system, does not appear to affect this conclusion. Only the values for the strictly comparable directions within the crystals are given in the table, and so far as these and the mean value are concerned, the crystals might just as well have been rhombic.

(3) The molecular refractions of the thallium salts stand out high above those of the other salts of the series, just as do the refractive indices.

As regards the monoclinic double salt series the following very similar rules are found to apply.

(1) The whole of the specific and molecular optical constants of the rubidium salt of any group are intermediate between those of the corresponding potassium and caesium salts belonging to the same group, that is, having the same *M*-metal and acid. The molecular refraction and dispersion increase at an accelerating rate with the rise of atomic weight of the alkali metal.

(2) The molecular refraction of the ammonium salt of each group is just slightly higher than the value for the

corresponding rubidium salt. Hence, the ammonium salts occupy the same position in the series as regards molecular refraction, that is, resistance of the molecule to light vibration, as they have been shown to occupy with respect to both molecular volume and the molecular dimensions in space (distance ratios). The individuality of the ammonium salts, however, is shown with respect to the molecular dispersion, which is almost as great as that of the caesium salts. Doubtless this is connected with the more extended nature of the whole group  $\text{NH}_4$ , as compared with a potassium atom.

(3) The molecular refraction and dispersion of the thallium salts, as exemplified by thallium zinc sulphate, are exceptionally high, as in the case of the simple salts.

**Refraction Equivalents in Solution.**—The molecular refractions of the potassium, rubidium, caesium, and ammonium sulphates and selenates (the thallium salts are too difficultly soluble) were determined for the state of solution in water, in order to compare the values with those for the crystalline state. A very interesting result was obtained, which illustrates in a beautiful manner to what fine detail of the optical properties the law of progression according to the atomic weight of the alkali metal, and the rule as to the position of the ammonium salt near the rubidium salt, are carried. The following table<sup>1</sup> expresses the results:—

*Comparison of the Refraction Equivalents for Crystalline and Dissolved States.*

Salt.	Mean Molecular refraction of Crystals.	Molecular Refraction in Solution.	Difference
$\text{K}_2\text{SO}_4$	32.04	33.21	+1.17
$\text{Rb}_2\text{SO}_4$	37.55	38.21	+0.66
$(\text{NH}_4)_2\text{SO}_4$	38.75	39.43	+0.68
$\text{Cs}_2\text{SO}_4$	47.48	47.27	-0.21
$\text{K}_2\text{SeO}_4$	38.50	39.65	+1.15
$\text{Rb}_2\text{SeO}_4$	44.06	44.63	+0.57
$(\text{NH}_4)_2\text{SeO}_4$	45.92	46.79	+0.87
$\text{Cs}_2\text{SeO}_4$	54.35	54.10	-0.25

<sup>1</sup> *Journ. Chem. Soc.*, 1906, 89, 1080.

The first column of figures gives the mean of the three Gladstonian refraction equivalents for the ray C corresponding to all three axes of the optical ellipsoid of each salt. The next column gives the molecular refractions of concentrated solutions (the mean in each case of several highly concordant determinations with different concentrations), obtained by determining both the refractive index and the density of each solution, and calculating for the ray C, knowing by direct previous determination the value for water, and assuming the truth of Gladstone's law.

The last column of the table compares the two results, and it will at once be observed that the potassium salt of each group shows a positive difference of slightly over a unit, the rubidium salt in each case a less positive difference, the ammonium salt almost the same, and the cæsium salt a very small negative difference. There is thus a regular progression in these small differences as the atomic weight of the alkali metal rises, the positive difference diminishing until at the cæsium salt it has passed zero and become slightly negative, while the ammonium salt behaves, as regards these minute differences, almost exactly (especially in the case of the more strictly comparable sulphate) like the rubidium salt of the same group.

This result has also an even more important consequence, for it affords the final proof of Gladstone's generalisation that "the refraction equivalent of a solution is the sum of the refraction equivalents of the solvent and of the substance dissolved." It shows that while slight differences in the molecular refractions are introduced by the change of state, such differences occur on both sides of zero, and that in the cases of isomorphous salts of metals of the same family group the differences follow the order of the atomic weights of the interchangeable metals.

**Axial Relationships of the Optical Ellipsoid.**—The difference of refractive power along different directions in the crystals of the various salts is very clearly indicated by the relative values of the three rectangular axes of the optical ellipsoid, either the indicatrix or its polar reciprocal the Fresnel ellipsoid. These ratios are compared in the next two tables; for the sake of variety the first gives the values for the rhombic series of the Fresnel velocity ellipsoid, while those of the second refer to the indicatrix of the monoclinic series. Quite similar results are afforded in either case if those for the other ellipsoid are compared instead. The value for the direction of the  $b$  crystallographic axis of the initial potassium salt is taken as unity in the first table referring to the simple rhombic series; and the value for the  $\beta$ -axis of the ellipsoid itself of the potassium salt is taken as unity in the second table referring to the monoclinic double salts. For in this latter series the ellipsoid is no longer fixed, as it is in the rhombic series, with its axes identical in direction with the crystallographic axes, except as regards the unique symmetry axis, which is identical with  $\beta$  in direction, and is the axis of rotation of the ellipsoid, with change of the  $R$ -metal or acid, already referred to.

#### RHOMBIC SERIES.

##### *Axial Ratios of Optical Velocity Ellipsoids.*

					$a$	$b$	$c$
$K_2SO_4$	...	...	...	...	0.9992 : 1		.0 9975
$Rb_2SO_4$	...	...	...	...	0.9862 : 0.9871		0.9869
$(NH_4)_2SO_4$	...	...	...	...	0.9742 : 0.9806		0.9820
$Cs_2SO_4$	...	...	...	...	0.9536 : 0.9547		0.9575
$Tl_2SO_4$	...	...	...	...	0.7922 : 0.7999		0.8030
$K_2SeO_4$	...	...	...	...	0.9975 : 1		: 0.9939
$Rb_2SeO_4$	...	...	...	...	0.9881 : 0.9895		0.9853
$(NH_4)_2SeO_4$	...	...	...	...	0.9837 : 0.9822		0.9688
$Cs_2SeO_4$	...	...	...	...	0.9593 : 0.9602		0.9596
$Tl_2SeO_4$	...	...	...	...	0.7817 : 0.7876		0.7836

## MONOCLINIC SERIES.

*Axial Ratios of Optical Indicatrix,  $\beta_{\text{salt}} = 1$ .*

Salt.			$\alpha$	$\beta$	$\gamma$
Potassium zinc sulphate	...	...	0.9961 . 1	· 1 0092	
Rubidium „ „ „	...	...	1 0000 : 1 · 0034	· 1 0096	
Ammonium „ „ „	...	...	1 · 0037 : 1 · 0065	: 1 0109	
Cæsium „ „ „	...	...	1 0127 : 1 0145	1 · 0175	
Thallium „ „ „	..	.	1 0740	1 0850	1 0900
Potassium zinc selenate	..	...	0 9960 : 1	1 · 0101	
Rubidium „ „ „	..	.	0 9988 : 1 0027	1 0099	
Ammonium „ „ „	..	...	1 0039 . 1 0078	1 0134	
Cæsium „ „ „	...	...	1 · 0096 · 1 0119	. 1 0152	

The following facts are at once apparent from a study of these tables.

(1) The axial ratios of the optical indicatrix, or of its polar reciprocal the velocity ellipsoid of Fresnel, for rubidium sulphate or selenate are intermediate between those for the sulphate or selenate of potassium and cæsium. When analogous directions are compared, the values for the rubidium salt are nearer to those of the potassium salt than to those for the cæsium salt. Hence, the progression in the axial values of the optical indicatrix, according to the atomic weight of the alkali metal, is an accelerating one.

This may be more interestingly expressed by saying that if the optical indicatrices of the potassium, rubidium, and cæsium salts of the same acid, either sulphuric or selenic, were constructed about the same point as origin, the ellipsoidal surface for the cæsium salt would contain within it that for the rubidium salt, separated by an appreciable interval, and this again would contain the indicatrix of the potassium salt at a less interval. The optical velocity ellipsoids of Fresnel would also similarly envelop each other, only in this case, that represented by the numbers in the first table, the ellipsoid of the potassium salt would be the outer one and that of the cæsium salt the inner one.

(3) The positions of ammonium sulphate and selenate are very close to those of the corresponding rubidium salts, just beyond them on the cæsium side. The indicatrix in each case would lie just outside and the Fresnel ellipsoid just within the analogous ellipsoid for the rubidium salt.

The monoclinic symmetry of ammonium selenate does not appear to affect this relationship, except that some rotation about the *b*-axis occurs, the dimensions being practically as if the salt were rhombic like the others. Doubtless if the rhombic form of ammonium selenate could be isolated in good crystals, the constants would be found to obey the rule of closeness to the rubidium salt values even more perfectly, and of course without this possibility of rotation.

(4) The ellipsoids of the thallium salts indicate the same outstanding optical character of thallium as was observed in the refractive indices. The indicatrices are relatively enormously expanded ones as compared with the salts of the three alkali metals and ammonium, and the Fresnel ellipsoids lie very considerably within the corresponding ellipsoids for the other salts.

Passing now to the second table referring to our typical zinc group of the monoclinic double salts, we observe the following very similar facts.

(1) The axial ratios of the optical ellipsoid of any rubidium salt of the monoclinic series of double salts are intermediate between those for the corresponding potassium and cæsium salts. The greater change accompanies the replacement of rubidium by cæsium, so that the progression according to atomic weight of the alkali metal is an accelerating one.

(2) The ammonium salt of any group possesses axial ratios of the optical ellipsoid which are intermediate between those for the rubidium and cæsium salts of the same group. The zinc selenate group shows them as far

removed from the rubidium salt as has yet been observed, just beyond half-way ; in other groups they approximate distinctly nearer to the values for the rubidium salt.

(3) The indicatrix of thallium zinc sulphate lies far outside the indicatrices of the other four salts of the group, indicating that the thallium double salts in general possess greatly expanded optical indicatrices compared with the other double salts of the series.

**Optic Axial Angles.**—It has already been mentioned that owing to the reversal of the sign of the double refraction, as a direct result of the operation of the law of diminution of double refraction with rise of atomic weight of the alkali metal, the simple rhombic sulphates display remarkable optic axial angle phenomena, involving a crossing of the plane of the optic axes at either the rubidium salt (sulphate) or the cæsium salt (selenate). The experimental observations were so interesting that the author was led to make a special study of the phenomenon of crossed-axial-plane dispersion, and the results of the investigation will be given in the next chapter. The phenomenon enters also into the optical character of a member of each of two groups of the double salts, owing to the effect of the rule of diminution of double refraction on groups already low in that property in the potassium salt, namely, the magnesium sulphate and selenate groups ; for cæsium magnesium sulphate and selenate also exhibit the phenomenon of crossed-axial-plane dispersion. These cases will likewise be referred to in the next chapter.

The other groups of the double salts are not affected by it, the amount of double refraction being greater at the start, in the potassium salt, so that the operation of the law of convergence of the extreme values of the refractive index does not reduce it even in the cæsium salt to the critical point at which two of the three indices become identical. The zinc groups are typical of these normal

groups, and their optic axial angles are thus truly comparable. They are given in the next table.

### ZINC GROUPS OF DOUBLE SALTS

*Optic Axial Angles 2Va.*

	KZn Sulphate	RbZn Sulphate	CsZn Sulphate	AmZn Sulphate	TlZn Sulphate
Li ...	68°17'	73°42'	74°30'	78°57'	69° 8'
C ...	68 16	73 40	74 27	78 58	69 12
Na ...	68 14	73 33	74 11	79 0	69 24
Tl ...	68 12	73 27	73 52	79 2	69 37
F ...	68 9	73 18	73 31	79 3	69 55
	KZn Selenate.	RbZn Selenate	CsZn Selenate	AmZn Selenate	
Li ...	66°12'	75°16'	83°33'	82° 5'	
C ...	66 13	75 14	83 30	82 5	
Na ...	66 15	75 8	83 6	82 7	
Tl ...	66 17	75 2	82 43	82 9	
F ...	66 20	74 55	82 14	82 10	

It will be observed that :

(1) The optic axial angle of the rubidium salt of either group is intermediate between the optic axial angles of the potassium and caesium salts. In the selenate group it is nearly the mean of the values for those two salts, but in the sulphate group it is nearer to the caesium salt value.

(2) The optic axial angles of the ammonium salts are not far removed from those of the caesium salts; in the zinc sulphate group they are somewhat higher, and in the zinc selenate group slightly lower.

(3) The optic axial angle of the thallium double sulphate lies between the optic axial angles of the corresponding potassium and rubidium salts.

It must be remembered that the optic axial angle of any one salt is dependent on the mutual relationships of the lengths of the three axes of the optical ellipsoid in that same salt, and that these are secondary effects of the total change of the ellipsoid in passing from one salt of the series to another; also moreover, that the whole ellipsoid in the case of the double salt series rotates about the symmetry axis at the same time, and to different extents for different wave-lengths of light. Further, the law of diminution of

the double refraction again exerts a profound influence on the optic axial angle and on the dispersion of the optic axes for different wave-lengths of light. Yet even so, the following table of the axial ratios of the optical indicatrix, in which  $\beta$  of each salt is taken as unity so that the ratios exhibit the net effect of all these influences on the optic axial angle, indicates a steady progression according to the atomic weight of the alkali metal.

*Axial Ratios of Indicatrix, for Zinc Group of Double Salts*

				$\alpha$	$\beta$	$\gamma$
Potassium zinc sulphate	..	..	..	0.9961	: 1	: 1.0092
Rubidium „ „	..	..	..	0.9966	: 1	: 1.0061
Ammonium „ „	..	..	..	0.9972	: 1	: 1.0043
Cæsium „ „	..	..	..	0.9983	: 1	: 1.0030
Thallium „ „	..	..	..	0.9899	: 1	: 1.0047
Potassium zinc selenate	..	..	..	0.9960	: 1	: 1.0101
Rubidium „ „	..	..	..	0.9961	: 1	: 1.0072
Ammonium „ „	..	..	..	0.9961	: 1	: 1.0056
Cæsium „ „	..	..	..	0.9977	: 1	: 1.0033

But the truly significant and dominant optical properties—the total change (expansion or contraction) of the axial dimensions of the optical ellipsoid, the rotation of the ellipsoid in the case of the monoclinic series, the magnitude of the double refraction, and the all-important property of refraction itself—have all been shown to be subservient to definite laws of progression according to the atomic weight of the alkali metal, as regards the salts of potassium, rubidium, and cæsium. It has also been shown to be the general law that the amount of optical change becomes less as the weight of the initial molecule increases, and therefore less as a rule in the selenate groups than in the sulphur groups. Also that the ammonium salts occupy positions close to the rubidium salts and on the cæsium side, while the thallium salts soar far above all these other salts of the series in their optical properties, owing doubtless to the fact that the thallium atoms offer far greater resistance to the propagation of light vibrations.

## CHAPTER XIII

### A GENERAL EXPLANATION OF CROSSED-AXIAL-PLANE DISPERSION OF THE OPTIC AXES.

THE phenomenon of crossed-axial-plane dispersion of the optic axes of crystals is not one which is very frequently exhibited, although it is not so rare as it was formerly supposed to be. It has been the author's good fortune to meet with no fewer than six new cases during his investigations, namely, rubidium sulphate, cæsium selenate, cæsium magnesium sulphate, the selenate of the same two metals, ammonium selenate, and the monoclinic form of ethyltriphenyl-pyrrholone, one of a homologous series of organic compounds differing by increments of  $\text{CH}_3$ , which were crystallographically investigated by the author in the year 1890.<sup>1</sup> The first four cases have been referred to in the last chapter. Ammonium selenate has been shown in Chapter X to be dimorphous, the ordinary form being monoclinic, and the other, which has only up to the present been found developed in mixed crystals with other members of the series, being rhombic like the common form of the simple salt series. The monoclinic form, however, also exhibits crossed-axial-plane dispersion of its optic axes.

In a memoir to the *Zeitschrift für Krystallographie*<sup>2</sup> the whole of these cases were compared, their phenomena

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<sup>1</sup> *Journ. Chem. Soc.* 1890, **57**, 714.

<sup>2</sup> 1906, **42**, 554.

analysed, and a general explanation for them arrived at. Subsequently, in a memoir to the Royal Society<sup>1</sup> the results were given of a detailed investigation of one of the oldest known cases, that of gypsum (selenite), the beautifully crystallised monoclinic hydrated sulphate of lime,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ; and the general explanation was shown to be equally valid in this case also, and, in fact, to deserve truly the name of a general explanation.

The requisite conditions for crossed-axial-plane dispersion, that is, separation of the optic axes of a biaxial crystal in two planes at right angles to each other, for the two extremes of the spectrum or for two different temperatures, have been found to be as follows:—

(1) The simultaneous occurrence of extremely small double refraction (nearness of  $\alpha$  and  $\gamma$  indices of refraction) and close approximation of the intermediate index  $\beta$  either to the  $\alpha$  or to the  $\gamma$  index. The latter condition is necessary for the possibility of crossing, and the former for wide separation of the optic axes in the two planes for the two ends of the spectrum, or for two different temperatures.

(2) Change of wave-length of the light employed at the ordinary temperature, or change of temperature while using light of the same wave-length, or both kinds of change simultaneously operating, must so act as to bring about equality, at a particular temperature for each wavelength, of two of the three refractive indices, namely, of the intermediate index  $\beta$  and of that one of the other two which is already nearest to equality with it.

The extreme delicacy of the situation when condition (1) is fulfilled will be appreciated when it is remembered that the spectral dispersion is different for each of the three refractive indices, and that the effect of change of temperature is also different along the three axial directions of the ellipsoid, thus further disturbing the balance.

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<sup>1</sup> *Proc. Roy. Soc., A*, 1908, **81**, 40.

As a change of only a few units in the fourth decimal place of the refractive index may be adequate, when all three indices are so close together as they are in these cases to start with, to provoke complete reversal of the relative positions of two of the three indices, it is readily conceivable that these directional slight differences of dispersion and of temperature effect may suffice to bring about the changes demanded by condition (2); that is, that such reversal may occur for light of the two ends\* of the spectrum or two different temperatures, and if so, that for an intermediate wave-length or temperature the identity of two indices, with consequential simulation of uniaxial optical properties, will occur.

There are roughly two classes of crystals showing crossed-axial-plane dispersion, namely, those which are particularly sensitive to change of temperature, and those which are more affected by change of wave-length of the illuminating light. These two classes, however, pass into each other so gradually that no hard and fast line of demarcation can be drawn. The five sulphates and selenates, and also ethyltriphenyl-pyrrholone, are intermediate cases more or less sensitive to both, and in the case of cæsium selenate, a very stable substance which can safely be heated to 250° C., the changes are so rapid that in the interval between the ordinary and that temperature each of the three axes of the optical ellipsoid in turn becomes the first median line.

But gypsum is pre-eminently characteristic of those most affected by variation of temperature, although, owing to its low decomposition temperature, the phenomena cannot be followed beyond 120° C. The other two well-known cases, brookite—the rhombic form of titanium dioxide,  $TiO_2$ —and the triple tartrate of potassium, sodium, and ammonium—obtained by crystallising mixed solutions of potassium sodium tartrate and ammonium sodium tartrate—are excellent examples of those extremely

sensitive to change in the colour of the light. Thus, while gypsum requires the section-plate perpendicular to the first median line (the acute bisectrix of the optic axial angle) to be warmed to about  $110^\circ$  in order to bring about the formation of the uniaxial figure, brookite and the triple tartrate show it at the ordinary temperature on illuminating the polariscope with light of all the colours of the spectrum in succession, as can readily be done with the aid of the author's spectroscopic monochromatic illuminator described in Chapter VI.

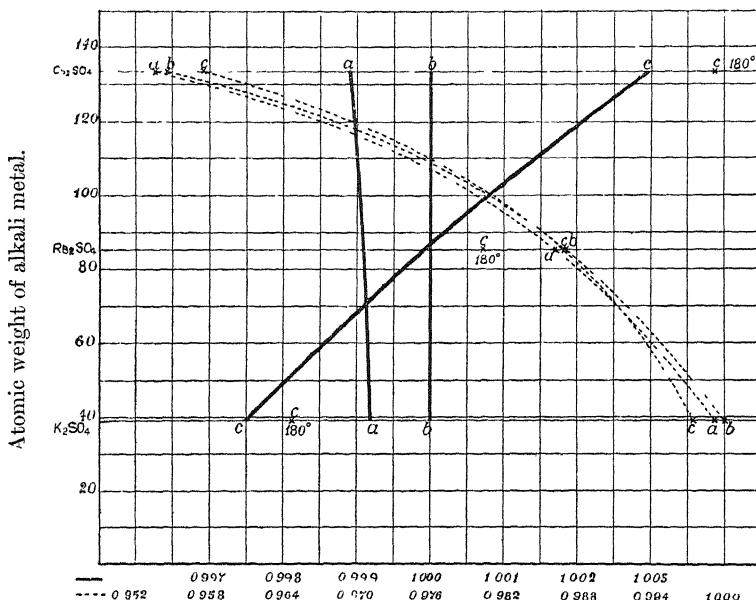


FIG. 48.—AXIAL RATIOS OF FRESNEL ELLIPSOID, FOR ALKALI SULPHATES.

The manner in which the generalisation applies in the cases of the sulphates and selenates and double salts of the rhombic and monoclinic series investigated by the author is briefly as follows. The double refraction has been shown in the last chapter to be already low at its maximum in the first member of any group, the potassium salt. The law of progression according to the atomic

weight of the alkali metal which was shown in the last chapter to apply equally to the optical as to the structural and crystallographic properties of the crystals, operates in the case of the property of double refraction in the direction of diminution ; that is, a convergence of the extreme indices  $\alpha$  and  $\gamma$  occurs as the atomic weight of the alkali metal increases. This fact will be rendered at once clear by the curves shown in Figs. 48, 49, 50, and 51.

Fig. 48 represents graphically the relations of the three axes of the Fresnel ellipsoid of the sulphates of potassium,

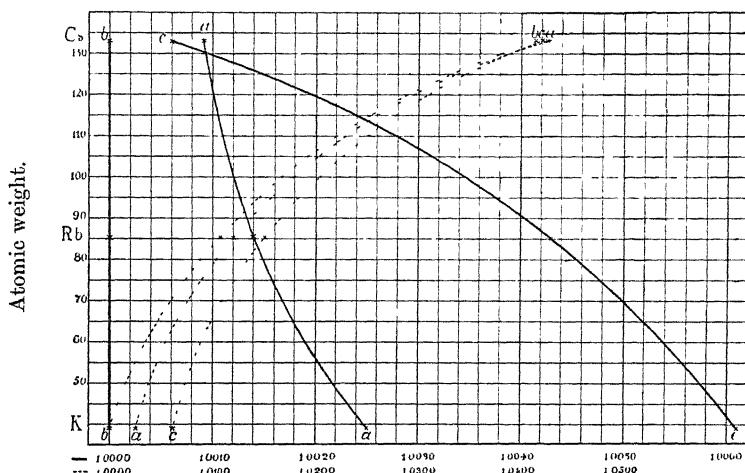


FIG. 49.—AXIAL RATIOS OF OPTICAL INDICATRIX, FOR ALKALI SELENATES.

rubidium, and cæsium, while Fig. 49 does the same for the relations of the three axes of the optical indicatrix or of the refractive indices of the selenates of the same three metals, and Fig. 50 for the zinc double selenate group. The double sulphates and selenates all afford such similar curves that Fig. 50 may be taken as a type of the whole series. Fig. 51 represents the relations in the magnesium selenate group in which, as well as in the corresponding sulphate group, the phenomenon of crossed-axial-plane dispersion is manifested. The dotted curves give the

total change in the axial lengths of the Fresnel ellipsoid (Fig. 48), or of the optical indicatrix, or of refractive index along those directions, in the cases of Figs. 49, 50, and 51; while the continuous curves give the relative values for each salt when the  $b$ - or  $\beta$ -value is taken as unity, and the latter perhaps show the convergence of the extreme values from the potassium to the cæsium salt most clearly.

The diminution of double refraction is shown by the dotted curves (best by those of Figs. 49, 50, and 51) to be

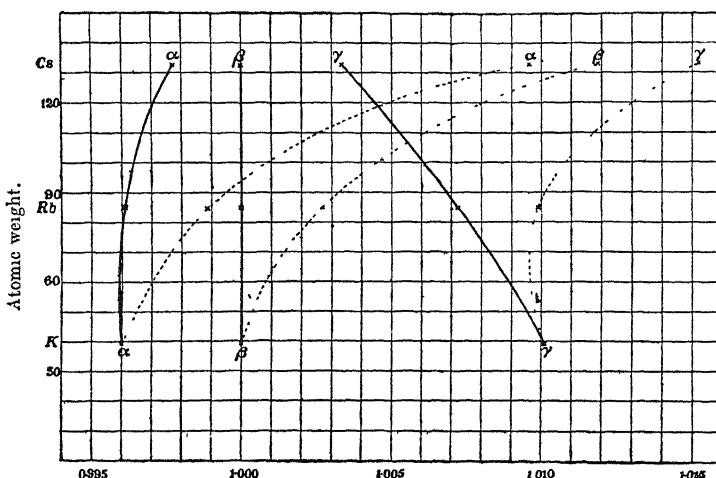


FIG. 50.—AXIAL RATIOS OF OPTICAL INDICATRIX, FOR ZINC DOUBLE SELENATES.

the result of a general diminution of refractive index with increase of atomic weight of the alkali metal, along all three axial directions of the optical ellipsoid, indeed in all directions within the crystal. But the amount of change, indicated by the slope of the curves, is seen to be different for the three directions, that for axis  $c$  or  $\gamma$  being notably less than the others. The result on the relations of the three is shown by the convergence of the curves as they rise in the diagram, in Fig. 48 towards the middle, the situation of the metal of intermediate atomic weight,

rubidium, but towards the top in Figs. 49, 50, and 51, where the atomic weight of the alkali metal, cæsium, is at its maximum. Now the intermediate index  $\beta$  is not the exact mean of the two others, but is either nearer to  $\alpha$ , in the cases of positive double refraction, or to  $\gamma$ , in negative crystals.

Fig. 50, representing the zinc group of double selenates, which is typical of all groups but those containing magnesium, shows the normal course of affairs, where the double refraction diminishes progressively and acceler-

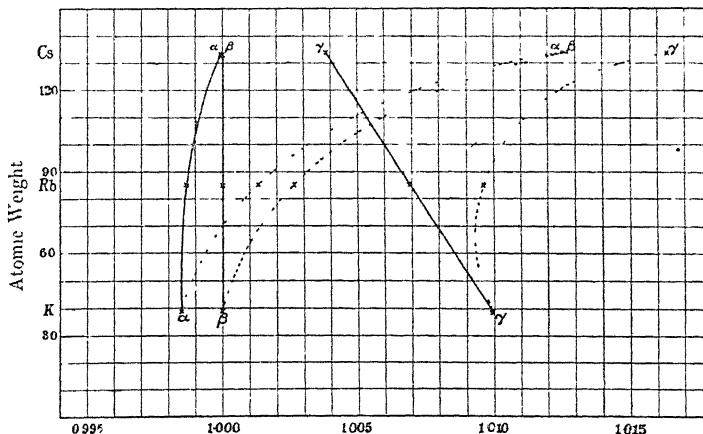


FIG. 51.—AXIAL RATIOS OF OPTICAL INDICATRIX, FOR MAGNESIUM DOUBLE SELENATES.

atingly towards the cæsium salts, without ever reaching zero. But in those groups in which the phenomenon of crossed-axial-plane dispersion is shown, represented by Figs. 48, 49, and 51, the first effect of the convergence of  $\alpha$  and  $\gamma$  is to bring two of the indices to identity; they are generally those which are already the nearer to each other, as shown in Fig. 51, although this is not necessarily the case, and it is the opposite in the sulphate and selenate groups, as shown in Figs. 48 and 49. This identity may happen to be exactly attained at the ordinary temperature at either the rubidium or the

cæsium salt; or at one or other of these salts a position very close to identity may be reached at the ordinary temperature, and, if the effect of rise of temperature is in the right direction, the position of actual identity may be attained on raising the temperature slightly.

Both these possibilities are realised in the salts mentioned. Identity of two indices,  $\alpha$  and  $\beta$ , which are already the closer in the initial potassium salt, is actually attained at the ordinary temperature for a specific wave-length in the blue in the cases of cæsium magnesium sulphate and cæsium magnesium selenate, as clearly shown in the latter case in Fig. 51; and the uniaxial cross and circular rings are exhibited by a section-plate perpendicular to the first median line in blue convergent polarised light. of this particular wave-length. For wave-lengths on each side of this one in the blue, biaxial interference figures are produced, the two optic axes being separated more and more for colours towards the red end of the spectrum in one plane (along one diameter of the field), and for colours towards the violet in the perpendicular plane (the diameter at right angles to the other). This is beautifully illustrated in Fig. 51, where the  $\alpha$  and  $\beta$  curves, both dotted and continuous, are seen to meet when the cæsium salt is reached.

In the sulphate group of the rhombic series of simple salts the critical position of identity is all but attained at rubidium sulphate at the ordinary temperature, as will be clear from the crossing of the  $b$  and  $c$  curves just beyond the level of this salt in Fig. 48, and absolutely so at  $40^\circ$  with production of the uniaxial figure for the red end of the spectrum, and at succeeding higher temperatures for the various colours, until even for violet light identity is reached at  $65^\circ$ . In the selenate group it is cæsium selenate which exhibits the critical condition and with it the crossing of the axial planes, the  $\alpha$  and  $c$  curves shown in Fig. 49 having just crossed each other and the  $c$  curve

passed within the  $a$  and  $b$  curves; the uniaxial cross and rings are produced at temperatures varying regularly from  $92^\circ$  to  $98^\circ$  for the various parts of the spectrum from the red to the blue.

This case of caesium selenate is one of great interest, for as already mentioned, within the comparatively short range of  $250^\circ$  of temperature, each axis of the optical indicatrix in turn becomes the first median line, and the sign of the double refraction changes first from negative to positive, and then back again to negative. For the first effect of heat in this case is to bring the  $c$  curve still further inside the  $a$  curve, bringing, in fact, the  $c$  curve to pass the middle position between  $a$  and  $b$ , and then to come nearer to  $b$ , the effect on the optic axial angle being to separate the optic axes further until they pass beyond an angle of  $90^\circ$ , and the first median line becomes the second and *vice versa*. On then examining the second section-plate perpendicular to what at ordinary temperature is the second median line, the axes are seen to approach the new first median line, and at  $92^\circ$  to  $98^\circ$ , according to the wave-length of the illuminating light, to unite in the centre of the field of the polariscope to produce the uniaxial figure (the  $b$  and  $c$  curves having met). They then recede along a new perpendicular diameter, and separate more and more until they pass out of the field of view. Picking them up at the temperature of  $150^\circ$  with a third section-plate perpendicular to a third bisectrix, the third axis of the optical ellipsoid, the optic axes may be followed by means of their rings as they approach each other in this new plane; eventually when the temperature of  $250^\circ$  is reached, the limit of safety with the polariscope, the sign of double refraction has again changed to negative, and the optic axial brushes themselves are clearly visible at an angle which within the crystal itself is less than  $90^\circ$ , and is still diminishing moment by moment.

The precise nature of the phenomena observed will perhaps be best rendered clear by taking one of the salts, say caesium magnesium selenate, as an example, and illustrating it by actual photographs of the interference figures observed in convergent monochromatic light in the polariscope-goniometer. Fig. 52 presents two series, each of six consecutively taken photographs for six particular wave-lengths of light, the first (upper) series at the ordinary temperature, and the second (lower) series when the section-plate was heated in the apparatus provided with the best Fuess polariscopical goniometer (the larger optic axial angle apparatus) to the temperature of  $78^{\circ}$ . The spectroscopic monochromatic illuminator was employed to afford the monochromatic light, and was invaluable in determining the exact wave-lengths for which the uniaxial figure was produced.

For red lithium light the optic axes are seen in the first figure separated widely in the horizontal plane; for yellow sodium light, green thallium light, and greenish-blue hydrogen light they are seen successively at smaller and smaller angles as they close in towards the centre of the field. The fifth figure exactly resembles that of an uniaxial crystal, and is that produced for the critical wave-length in the blue, 0.000466 millimetre, when the two optic axes have coalesced into a single optic axis, and the ellipses, lemniscates, and rings have become concentric circles. The sixth figure represents what is seen in violet hydrogen light, the axes having now separated again, but along the vertical diameter of the field instead of the horizontal.

The second series has been chosen for the temperature of  $78^{\circ}$ , at which the uniaxial figure is produced for sodium light, the axes being still separated in the horizontal plane for wave-lengths on the red side, but in the vertical plane for wave-lengths on the violet side. For on heating the section-plate the uniaxial figure travels through the

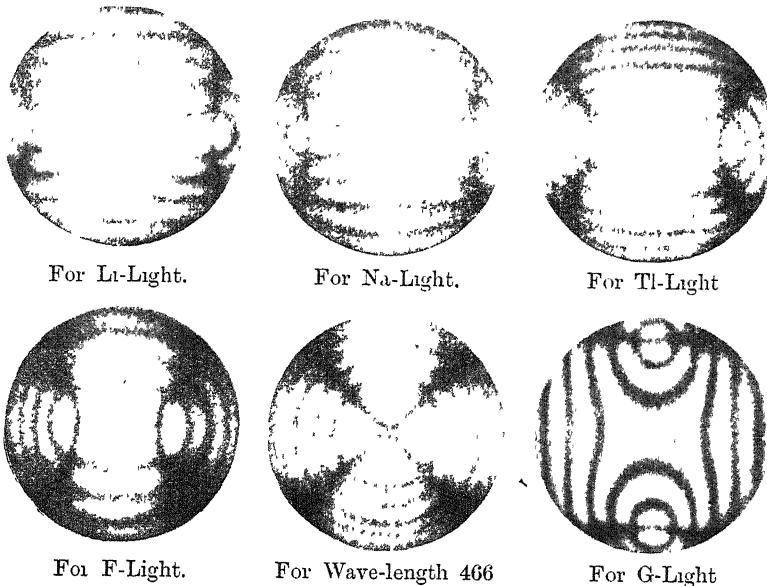
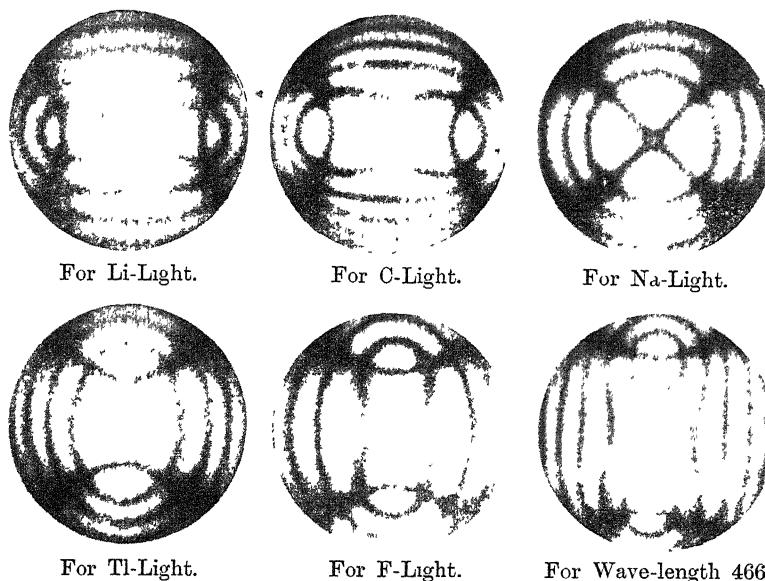
*Series 1—Ordinary Temperature.**Series 2.—Temperature 78°.*

FIG. 52.—INTERFERENCE FIGURES OF CÆSIUM MAGNESIUM SELENATE.

spectrum, being produced at  $34^{\circ}$  for F-light,  $60^{\circ}$  for Tl-light,  $78^{\circ}$  as stated for Na-light,  $91^{\circ}$  for C-light, and lastly at  $94^{\circ}$  for lithium light. At  $97^{\circ}$ , beyond which it is not safe to heat the crystal, on account of the possibility of loss of its water of crystallisation and accompanying opacity, the optic axes are separated altogether in the vertical plane, for all wave-lengths of the visible spectrum, the angle being very small for red light, but so large for violet light that the axes themselves have passed beyond the upper and lower margins of the field.

Section-plates perpendicular to the first median line to show these phenomena require to be very thick—half a centimetre or more—in order to afford sharp interference figures, on account of the extremely low double refraction, which has been shown to be one of the conditions for the production of the phenomenon.

Very similar phenomena are afforded by the other four salts of the two series under discussion, and by monoclinic ethyltriphenyl-pyrrholone, the differences being only in the details, and the temperatures at which the uniaxial figures are produced. Cæsium magnesium sulphate especially closely resembles its selenate analogue just described, exhibiting the crossing for a wave-length in the blue, in this case  $0\cdot000450$  millimetre, at the ordinary temperature.

The interesting case of gypsum has lately been demonstrated by the author to the Royal Society, and to the British Association in his evening Discourse at the Winnipeg meeting, in a novel manner. A fine projection polariscope was used, furnished with a pair of magnificent calcite Nicol prisms as polariser and analyser,  $2\frac{1}{4}$  inches minimum clear aperture, made by Mr. Ahrens from the original and now-exhausted stock of large Iceland spar; it is also provided with a new lens-system and series of special fittings, comprising crystal-holders, stages, signal-slits, optic-axial-angle goniometers with convergent systems, a direct-vision spectroscope, and many other

accessories for crystallographic projection. The best features of the Lewis Wright polariscope, without any of the restricting tubes, and of the Fuess apparatus, have been embodied together with many original features ; and the whole of the lenses and accessories are mounted on separate adjustable pedestals, rising from sliders which may be arranged interchangeably anywhere in the basal lathe-bed, in which the nicols are similarly adjustable. It is shown in position in front of the electric lantern, with the Mitscherlich experiment arranged, in Fig. 53. The two lenses and rotating object-stage, seen in the recess underneath, replace the lenses, crystal-stage, and convergent systems shown in position, when it is desired to project objects in parallel light.

The essence of the author's new mode of projecting this experiment is that no extraneous heat is employed, the heat rays accompanying the light rays being ample to effect the purpose, even although a water jacket two inches thick is placed between the lantern condenser and the polarising Nicol, in order to cut off the greater amount of the heat rays and thus to protect the balsam of the nicols. The lens system is so accurately calculated to produce the focus of the convergent rays precisely on the centre of the crystal, as a brilliant spot not exceeding a couple of millimetres in diameter, that the large crystal usually employed for the purpose of this experiment is unnecessary, and the usual large metallic holder with flap for heating it by a spirit lamp or small Bunsen flame is discarded as altogether superfluous. A miniature crystal section-plate six millimetres square, but two millimetres thick on account of the low double refraction and the desirability of obtaining a sharp interference figure, is employed. It is mounted in a thin platinum-foil similarly small carrier, a lip of which is gripped by a small wooden holder held in turn by the usual metallic crystal-holder of the apparatus. As thus mounted there is very little conduc-

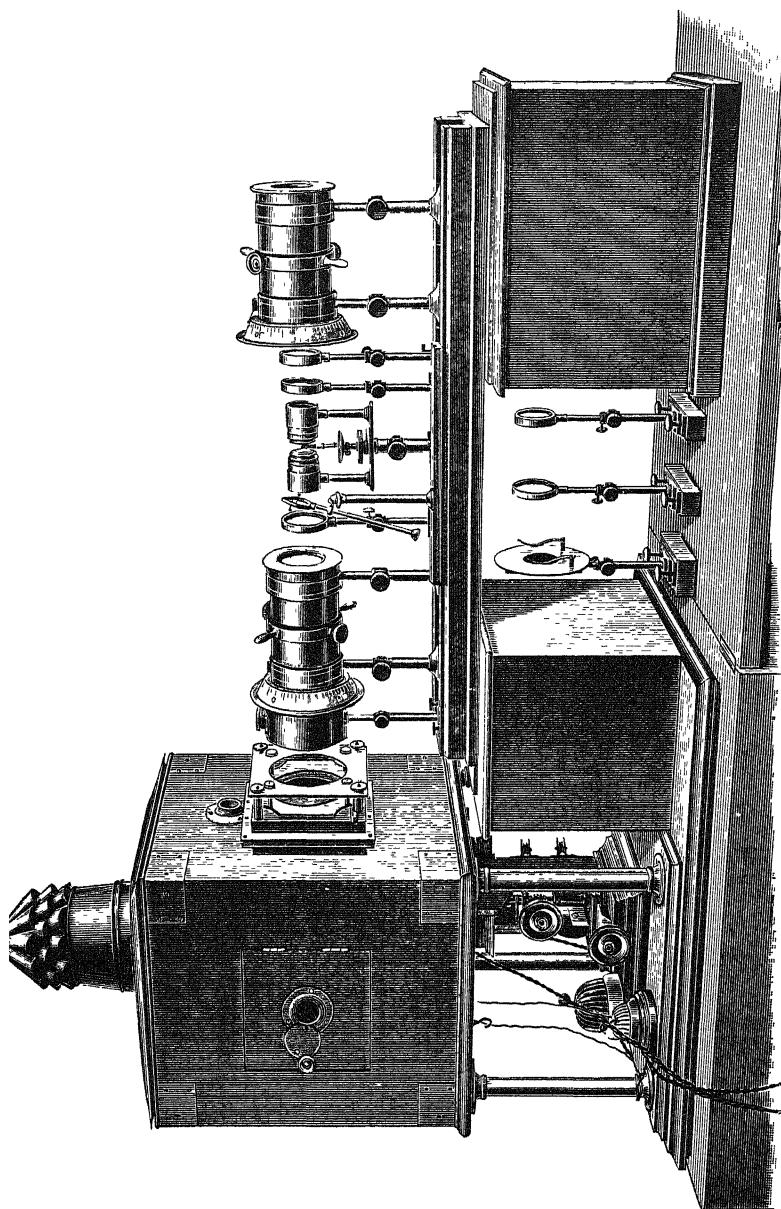


FIG. 53.—THE PROJECTION POLARISCOPE ARRANGED FOR THE MITSCHERLICH EXPERIMENT.

tion of heat away from the crystal, and the heat-rays accompanying the light, and surviving after the greater part have been removed by the water layer, are ample to cause the crossing of the optic axes.

As soon as the electric arc of the lantern is switched on, the rings surrounding the axes make their appearance on the right and left hand edges of the field, the centre begins to light up with colour as the lemniscates enveloping the rings alternately form and break up their figure-of-eight, and ring after ring in brilliant spectrum tints comes into the field ; very soon the hyperbolie brushes marking the axes themselves appear, rapidly moving towards the centre of the field, while the surrounding rings and lemniscates exhibit an ever changing and more and more brilliant display of spectrum colours in succession. Eventually the brushes coalesce into a rectangular cross, and the surrounding spectrum ellipses which have succeeded the lemniscates become concentric circles. Then, quite as steadily, the cross opens out again—but along the vertical diameter of the field, as the temperature rises above the crossing point, which varies in different crystals from  $105^{\circ}$  to  $115^{\circ}$  C.—into hyperbolie brushes whose vertices become more and more separated along the vertical plane. As soon as they are well separated in this plane, the crystal can be saved from becoming incinerated to plaster of Paris (gypsum losing its water of crystallisation at  $120^{\circ}$  or thereabouts) without impairing the beauty of the experiment, by interposing a fairly thick glass plate, if necessary a little obliquely, which just deranges the focus of the converging system sufficiently to reduce the temperature of the crystal, when the axes retrace their steps past the crossing point. Or an opaque screen may be rapidly introduced and removed intermittently to effect the same object, or still more simply, a gentle current of air may be blown past the crystal.

The author's investigation of gypsum included the

re-determination of the refractive indices at the ordinary temperature and their determination at  $105^{\circ}$ , with the aid of two  $60^{\circ}$ -prisms accurately cut in the theoretically desirable directions out of the same crystal to afford respectively  $\alpha$  and  $\beta$ , and  $\beta$  and  $\gamma$ . At the crossing temperature in the neighbourhood of  $100^{\circ}$  the former prism afforded only a single image of the spectrometer-goniometer signal-slit, the two images close together, representing  $\alpha$  and  $\beta$ , with which the experiment started at the ordinary temperature, having gradually approached each other as the temperature rose and eventually overlapped; so that at the critical temperature, corresponding to that at which a section-plate perpendicular to the first median line shows the uniaxial figure, the two images are identical. This now single image, however, is distinguished from one afforded by an ordinary case of single refraction, say the usual refracted image given by a glass prism, inasmuch as it really consists of two images, one of which is extinguished by the nicol prism at  $0^{\circ}$  and the other at  $90^{\circ}$ , the one constantly waxing as the other is waning when the nicol is rotated. On continuing the heating the two images separate again, but on opposite sides of each other, and that image which formerly corresponded to the lowest refractive index  $\alpha$  now represents  $\beta$ , while that which had hitherto afforded  $\beta$  becomes the  $\alpha$  image.

This interesting behaviour of the images afforded by the prism yielding the two indices of refraction which become identical, thus giving rise to the crossing of the optic axial planes, was carefully followed in all the five cases of sulphates and selenates and double salts of the rhombic and monoclinic series which have been mentioned as exhibiting this phenomenon, and the ascertained cause of the phenomenon was thus experimentally verified by actual investigation of the refractive index phenomena at higher temperatures. It was carried out with the aid of the most efficient form of heating apparatus provided with

the large No. 1a Fuess spectrometer-goniometer. In the case of gypsum, moreover, in order to avoid all possible source of error due to different natural crystals exhibiting slightly different optical constants, as is often the case with natural products, the two section-plates perpendicular to the first and second median lines were also cut from the same single well-developed crystal as furnished the 60°-prisms, so that all the optical constants were determined with one and the same crystal. The results were thus both concordant and eminently trustworthy. Three other different crystals were also investigated, with practically identical results, the only differences being those mentioned below as to the absolute temperatures at which the phenomena occur.

The work on gypsum fully confirms the conclusions derived from the investigation of the rhombic and monoclinic sulphates, selenates, and double salts, that the phenomenon of crossed-axial-plane dispersion of the optic axes is due to very low double refraction, combined with close approximation of the intermediate index of refraction to one of the extreme indices ; and to the fact that change of wave-length of the light or change of temperature, or both, cause the intermediate index to approach still nearer to the extreme one in question until it becomes identical with it, and eventually to pass it, the relative positions of the two thus becoming reversed.

The uniaxial rectangular cross and circular rings are produced at the critical point of identity, which is a function of both wave-length and temperature. In the case of gypsum temperature plays by far the preponderating rôle, and the curious fact, first observed by von Lang but without an exact determination of the wave-length, was established that the temperature has a maximum for a particular wave-length near the middle of the spectrum, 0.000573 mm. in the greenish-yellow not far from the sodium D-lines. But the range of temperature which

includes the production of the uniaxial figure for all the colours of the spectrum in succession does not exceed  $4^{\circ}$ . The absolute temperatures of crossing for the four different crystals investigated varied  $9^{\circ}$ , the maximum temperature for wave-length 573 varying from  $105^{\circ}5$  to  $114^{\circ}5$ , these being corrected temperatures; the correction for conduction away of heat by the crystal holder of platinum is quite considerable, as much as  $7^{\circ}$ , and if the ordinary brass holder had been used it would have been much more. This important correction is one which previous observers appear not to have applied. In an actual experiment the uniaxial figure was produced first for violet G-light at  $102^{\circ}5$ . Then at  $104^{\circ}5$  it was produced both for greenish-blue F-light and red Li-light. Next for both sodium and thallium light it was produced about  $105^{\circ}$ , namely, at  $105^{\circ}2$  for Na-light and  $105^{\circ}1$  for Tl-light. And lastly at  $105^{\circ}5$  it was produced for the critical wave-length 573 in the greenish-yellow. When this was attained, rotation of the prism-circle of the monochromatic illuminator either way, so as to feed the polariscope with light on either side of wave-length 573, caused the rectangular cross to open out into hyperbolæ the vertices of which were separated in the vertical plane.

With the concordant results of this investigation of the interesting and historic case of gypsum, observed so long ago as the year 1826 by Mitscherlich, and demonstrated by him to the Berlin Academy, the experimental proof of the explanation of the phenomenon of crossed-axial-plane dispersion of the optic axes, as first given by the author as the result of the investigation of the sulphates, selenates, and double salts of the rhombic and monoclinic series, may now be said to be completely established.

## CHAPTER XIV

### RESULTS OF THE THERMAL INVESTIGATION OF THE SULPHATES.<sup>1</sup>

IT was obviously important to supplement the optical investigations, described in the last two chapters, by determinations of the coefficients of thermal expansion in the various directions in the crystals, in order to ascertain whether the symmetry of the structure and the law of progression according to atomic weight of the alkali metal were reflected in the thermal deformation. For otherwise it might be open to question whether the results for any particular temperature were not fortuitous ones, and that results bearing an altogether different complexion might be afforded if the experiments were made at other temperatures. It has been shown throughout the foregoing description of the optical properties that none of the determinations have been confined to the ordinary temperature, but that on the contrary they have been repeated at other higher temperatures; and that the results, as to the effect of atomic weight on the constants, have been found to be independent of the temperature. Moreover, it is well known that the ellipsoid of thermal conductivity or that of thermal expansion is so far similarly orientated to the optical ellipsoid, that in crystals of the rhombic system its axes are identical in direction with the three rectangular crystallographic axes; and that in the monoclinic system one axis of the thermal ellipsoid is identical with the symmetry axis perpendicular to the unique plane of

crystal symmetry, while the other two axes lie at right angles to each other in that plane, that is, the thermal-ellipsoid may rotate about the symmetry axis just like the optical one.

While thus the positions of the thermal axes in the rhombic series will be fixed, their relative dimensions may bear no relation whatever to those of the optical ellipsoid. Also it will be obvious that the crystallographic axial ratios  $a:b:c$  are functions of the temperature, as there is no necessary relation between the lengths of the crystallographic axes and those of the ellipsoid of thermal dilatation. But the axial angles are all  $90^\circ$  whatever the temperature. The same applies to the monoclinic series, except as regards the inclined axial angle  $\beta$ , and with the additional proviso that the position of the ellipsoid as regards the amount of its rotation about the symmetry axis, with respect to the crystallographic axes which lie in the symmetry plane, may bear no relation whatever to the position of the optical ellipsoid, the axis of rotation being the only thing remaining constant; and even the length of that bears no relation to that of the optical ellipsoid or to the crystallographic axial ratio which compares the length of this crystal axis with that of either of the other two. Hence, as the other two thermal axes lying in the symmetry plane may also have any lengths whatsoever, not only are the axial ratios  $a:b:c$  functions of the temperature, but also the axial angle  $\beta$  is dependent on the temperature. The right angles  $\alpha$  and  $\gamma$  are, however, always exactly  $90^\circ$  whatever the temperature.

The monoclinic series of double sulphates and selenates are not suitable for thermal investigation, on account of the ease with which many of the salts, notably the potassium ones, lose their water of crystallisation. The simple rhombic selenates are also unsuitable on account of their deliquescence, the caesium salt in particular being so very hygroscopic as to serve as an excellent desiccating

agent. But the rhombic simple sulphates are free from these defects, the slight deliquescence of caesium sulphate having been overcome by utilising only very dry days for the work with this salt, and employing the inner air-bath of the interference dilatometer described in Chapter VIII, which was employed for this investigation, indeed designed for it, as a desiccating chamber previous to the determinations.

The thermal work has therefore consisted in the determination of the coefficients of linear expansion of potassium, rubidium, and caesium sulphates, along the three rectangular directions of the crystallographic axes. Ammonium sulphate was not included for the obvious reason of the ease with which dissociation occurs on heating this salt, which would render any such determinations of doubtful trustworthiness.

The mode of carrying out the determinations, and the details of the interference dilatometer, have already been fully entered into in Chapter VIII and, as stated on p. 71, it only remains in this chapter to give the results of the sixty-four determinations which were carried out successfully, each of which occupied five to six hours.

The following are the results for the linear coefficients of expansion.

*Mean Coefficients of Linear Expansion,  $a+bt$ , between  $0^\circ$  and  $t$ .*

POTASSIUM SULPHATE.

For the direction of the axis  $a$  . . .  $0\ 000\ 036\ 16 + 0\ 000\ 000\ 014\ 4t$ .

“ “ “ “  $b$  . . .  $0\cdot000\ 032\ 25 + 0\ 000\ 000\ 014\ 1t$ .

“ “ “ “  $c$  . . .  $0\cdot000\ 036\ 34 + 0\ 000\ 000\ 041\ 3t$ .

RUBIDIUM SULPHATE.

For the direction of the axis  $a$  . . .  $0\ 000\ 036\ 37 + 0\ 000\ 000\ 020\ 3t$ .

“ “ “ “  $b$  . . .  $0\ 000\ 032\ 14 + 0\cdot000\ 000\ 018\ 4t$ .

“ “ “ “  $c$  . . .  $0\ 000\ 034\ 63 + 0\ 000\ 000\ 038\ 0t$ .

CAESIUM SULPHATE.

For the direction of the axis  $a$  . . .  $0\ 000\ 033\ 85 + 0\cdot000\ 000\ 021\ 4t$ .

“ “ “ “  $b$  . . .  $0\cdot000\ 031\ 95 + 0\cdot000\ 000\ 018\ 2t$ .

“ “ “ “  $c$  . . .  $0\cdot000\ 035\ 90 + 0\cdot000\ 000\ 041\ 4t$ .

The cubical coefficients are next compared in the following table.

*Mean Coefficients of Cubical Expansion, between 0° and t°.*

For potassium sulphate	...	0 000 104 75 + 0·000 000 069 8t
„ rubidium sulphate	...	0·000 103 14 + 0·000 000 076 7t.
„ caesium sulphate	...	0 000 101 70 + 0·000 000 081 0t.

The above mean coefficients are those represented by the formula  $\alpha + bt$ , where  $\alpha$  and  $b$  are the two constants of the general formula for the length explained on page 71 of Chapter VIII.

The actual coefficients of cubical expansion,  $\alpha$ , at any temperature  $t$ , and also the mean coefficients of cubical expansion between any two temperatures whose mean is  $t$ , are the following:—

$$Values \ of \ \alpha = \alpha + 2bt.$$

$\alpha$ for $K_2SO_4$ ..	$0\ 000\ 104\ 75 + 0\cdot000\ 000\ 139\ 6t$ , or $10^{-8}(10475 + 13\ 96t)$ .
„ $Rb_2SO_4$ ..	$0\cdot000\ 103\ 14 + 0\cdot000\ 000\ 153\ 4t$ , or $10^{-8}(10314 + 15\cdot34t)$
„ $Cs_2SO_4$ ..	$0\ 000\ 101\ 70 + 0\ 000\ 000\ 162\ 0t$ , or $10^{-8}(10170 + 16\cdot20t)$ .

These tables for the cubical expansion exhibit the most striking result of the thermal investigation, which may be stated as follows:—

(1) The coefficients of cubical expansion of the normal rhombic sulphates of potassium, rubidium, and caesium exhibit a progression corresponding to the progression of the atomic weights of the three respective metals. This is true of both the constants  $\alpha$  and  $b$  in the general expression for the coefficient of cubical expansion for any temperature  $t$ ,  $\alpha = \alpha + 2bt$ , the values of each constant for the rubidium salt being intermediate between the corresponding values for the potassium and caesium salts.

Other subsidiary facts brought to light are as under:—

(2) The order of progression of the two constants is inverted;  $\alpha$ , the coefficient for 0°, diminishes with increasing atomic weight of the metal, while  $b$ , half the increment of the coefficient per degree of temperature, increases.

(3) In consequence of rule 2, the coefficients of cubical expansion of the three salts converge, with rise of temperature, and attain equality in pairs in the neighbourhood of  $136^{\circ}$ , which is the actual temperature at which potassium and caesium sulphates expand equally; the actual temperature for identity of cubical expansion of potassium and rubidium sulphates is  $114^{\circ}$ , and for equality of expansion of rubidium and caesium sulphates  $168^{\circ}$ .

This will be clearer with the aid of the following table of actual expansions for a few selected temperatures up to  $200^{\circ}$ , and of the accompanying graphical expression of them in Fig. 54.

*Coefficients of Cubical Expansion for Various Temperatures from  $0^{\circ}$  to  $200^{\circ}$ .*

Salt.	$0^{\circ}$	$50^{\circ}$	$100^{\circ}$	$114^{\circ}$	$136^{\circ}$	$150^{\circ}$	$168^{\circ}$	$200^{\circ}$
$K_2SO_4$	$10^{-8} 10475$	11173	11871	12066	12373	12569	12820	13267
$Rb_2SO_4$	$10^{-8} 10314$	11081	11848	12065	12400	12615	12891	13382
$Cs_2SO_4$ ..	$10^{-8} 10170$	10980	11790	12017	12373	12600	12891	13410

Beyond the temperature of equal expansion of any two salts, divergence of the curves occurs. The chief point to observe is, however, that the change is a continuous one, as represented by the continuity of the curves, which are really straight lines, and that the progression according to the atomic weight of the metal is thus a steady one. If the coefficients for the three salts had not been so close to each other at the start, at  $0^{\circ}$ , the crossing point would never have been attained, and the result would have been merely that the increase of cubical expansion with rise of temperature suffered a steady diminution all through the series of three salts. But owing to the closeness to equality of the expansions of the three salts at  $0^{\circ}$ , the law of increase of the half-increment  $b$  per degree with rise of atomic weight soon reverses the diminishing effect of the constant  $a$ , and thus brings about the reversal of the

order of the salts as regards expansion, say at  $200^{\circ}$  as compared with  $0^{\circ}$ . The effect is, indeed, remarkably like that produced by the diminution of optical double refraction by rise of atomic weight, and the similarity of the curves in Fig. 48 indicating this property for the same three alkali sulphates, given on page 162, will at once be perceived. In both cases, however, the effects are due to steady regular changes corresponding to the regular progression of the atomic weights of the three alkali metals.

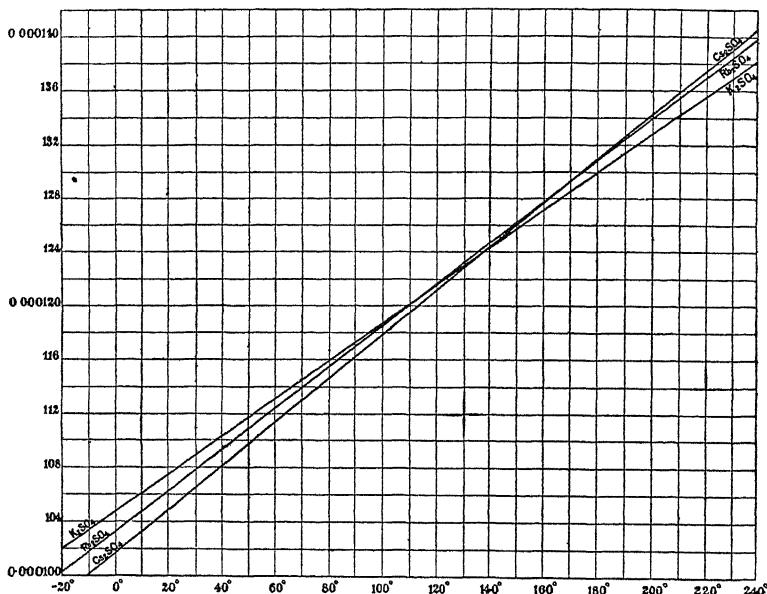


FIG. 54.—GRAPHICAL EXPRESSION OF CUBICAL EXPANSIONS.

As regards the directional changes, that is, the linear coefficients of expansion along the three crystallographic axial directions of the salts, it will be observed that :—

(4) The thermal expansion is of the nature of an expansion in all directions in the crystals of the three sulphates.

(5) The differences between the coefficients of linear expansion along the three crystallographic axial directions of any one salt, although only amounting to one-eighth of

the total coefficient, are large compared with the differences between the values for the same direction of the three salts.

(6) The operation of result 5, together with the fact that the replacement of one metal by another is accompanied by considerable modifications of the relations of two of the three values for the original salt—those corresponding to the axes  $a$  and  $c$ —prevent the coefficients of linear expansion for any one direction of the three salts from exhibiting any progression according to the atomic weights of the three metals. Those directional perturbations are, however, mutually compensative, so that the effect of the interchange of the metals is clearly exhibited by the solid deformation—the cubical expansion—the coefficients of which show the progression expressed in result 1, following the order of the atomic weights of the alkali metals.

(7) The increment of the linear coefficient of expansion for the direction of the vertical axis  $c$  of each salt is at least twice as large as the increment for the other two axial directions  $a$  and  $b$ , for which the increments are nearly equal. This thermal property is analogous to the optical behaviour, the refractive power being diminished by rise of temperature much more in the direction of the axis  $c$  than in the two other directions.

(8) The chief of the directional perturbations referred in result 6 consists of a reversal, for temperatures below  $50^\circ$ , of the directions of the maximum and intermediate axes of the thermal ellipsoid for rubidium sulphate, compared with their directions in the potassium and caesium salts. The maximum thermal axis is the crystallographic axis  $c$  for the two latter salts, but the axis  $a$  for the rubidium salt. A similar reversal of the first median line, the maximum axis of the optical ellipsoid (indicatrix) from  $c$  to  $a$  occurs for the same temperatures in the case of rubidium sulphate. The maximum thermal axis is identical in all three salts with the acute bisectrix of the optic axial angle.

(9) At higher temperatures the same relations, both

thermal and optical, obtain for the potassium and cæsium salts. But owing to the increment of expansion along the axis  $c$ , referred to in result 7, being so much greater than for the other directions, the intermediate expansion along  $-c$  for rubidium sulphate attains equality at  $50^\circ$  with the expansion along  $a$ , and beyond this temperature  $c$  becomes the maximum thermal axis for this salt, as it is for the other two sulphates. Consequently, at  $50^\circ$  the crystals of rubidium sulphate behave as if they were thermally uniaxial. At temperatures varying  $10^\circ$  on each side of  $50^\circ$  for different wave-lengths of light, rubidium sulphate crystals also simulate uniaxial optical properties.

A most striking parallelism is thus apparent between the optical and thermal properties of the three sulphates of potassium, rubidium, and cæsium, and it is of the deepest interest that all the complicated directional changes and relationships involved, which would otherwise be quite inexplicable, are the direct result of the few definite rules, connecting these properties with the progression in the atomic weight of the alkali metals, which have now been established. While the directional (that is the linear) coefficients of expansion and their increments have thus been shown to offer a remarkable analogy to the directional optical results, the cubical coefficients of expansion have been shown to exhibit, as the net summational effect of the whole of the directional changes, the progression according to the atomic weight of the metal in the clearest possible manner. The author has therefore concluded, with reference to the thermal investigation, that :—

*The thermal deformation constants of the crystals of the normal sulphates of potassium, rubidium, and cæsium exhibit variations, which, in common with the morphological, optical, and other physical properties previously investigated, follow the order of progression of the atomic weights of the alkali metals which the salts contain.*

## CHAPTER XV

### GENERAL RESULTS OF THE INVESTIGATIONS.

THE chief results of the investigations concerning the relations between chemical composition and crystalline character may now be summarised advantageously. The following main generalisation, which includes the whole of the crystal properties, has been abundantly proved:—

*The crystals of the different members of the rhombic series of isomorphous sulphates and selenates of the alkali metals,  $R_2\frac{S}{Se}O_4$ , and those also of the monoclinic series of double sulphates and selenates,  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ , whilst conforming to the same symmetry—that of their particular isomorphous series—and exhibiting the same facial forms inclined at angles which never differ by more than one or two degrees, exhibit progressive variations in their exterior geometrical configurations, interfacial angles, and crystallographic elements, in their internal structural properties and constants of which the external form is only the outward symbol, in their optical characters, and in their thermal behaviour; and these variations follow the order of progression of the atomic weights of the three alkali metals belonging exclusively to the same family group of the periodic classification, potassium, rubidium, and caesium, which by their interchange give rise to the series. The variations are, therefore, functions of*

*the atomic weight of the alkali metal, and they have been shown to be usually functions which involve higher powers of the atomic weight than the first. It has been further shown that: Similar variations attend the replacement of sulphur by selenium in the acid radicle present in the salts.*

So generally true have these fundamental conclusions proved to be, throughout not only the simple sulphates and selenates, but also throughout the whole of the eight groups of the double sulphates and the corresponding groups of double selenates which have already been completed,—all of which, owing to the vastly predominating influence on the crystal properties exercised by the alkali metal R (the influence of the *M*-metal being surprisingly small), offer so many independent confirmations of the truth of the generalisation,—that the author has felt justified in concluding that the latter is in truth a general law of nature, and has defined it in the following terms:—

*The whole of the morphological and physical properties of the crystals of an eutropic-isomorphous series are functions of the atomic weights of the interchangeable chemical elements, belonging exclusively to the same family group of the periodic classification, which give rise to the series.*

The term “eutropic” is introduced to qualify the isomorphous series in accordance with the precise definition given on page 125 in Chapter XI, in order to limit the meaning of the term “isomorphous,” as used in the above statement of the definite law of progression according to atomic weight, to the cases to which alone it applies, namely, to series of which the members are formed by the interchange of elements belonging strictly and exclusively to the same family group as defined by Mendeléeff.

Remembering this precise qualification and limitation, the fundamental law may be stated in the following further manner, which eliminates any idea that atomic weight,

as such, has any peculiar significance, other than being the most convenient expression of the essential difference between the atoms of the various elements and of their different, possibly additive, electronic-corporeal constitution.

*The difference in the nature of the atoms of the chemical elements of the same family group which is manifested in their regularly varying atomic weights, is also expressed in the similarly regular variation of the characters of the crystals of an eutropic-isomorphous series of salts of which these elements are the interchangeable constituents.*

The results of the investigations of these two series of such different chemical nature and crystalline symmetry, the one a simple anhydrous salt series of orthorhombic symmetry, and the other a monoclinic double salt series containing six molecules of water of crystallisation, are thus remarkably similar, and lead to the same conclusion as regards the effect of replacing potassium by rubidium, and the latter by caesium. A more or less specific character is imparted to any two corresponding sulphate or double sulphate and selenate or double selenate groups, on account of the fact that the replacement of sulphur by selenium becomes less powerful in modifying the crystallographic characters as the weight of the initial molecule increases ; that is, as the atomic weight of the metal present in the original sulphate increases. Hence, the results for any two corresponding sulphate and selenate groups are not represented by parallel lines, but by two converging lines. The interesting and important fact, however, stands out boldly, that while each group thus exhibits specific idiosyncrasies, the mutual relations of the members of the one group are identical with those of the members of the other. Moreover, the effect of replacing sulphur by selenium is invariably to produce variation in the morphological and physical properties of a similar

character to that produced when a lighter is replaced by a heavier alkali metal. Even the sign of these similar changes is the same in the cases of the molecular distance ratios and the optical constants. But it is reversed as regards the crystal angles, owing to the fact that different directions in the crystal structure are predominatingly influenced by the metal and by the sulphur or selenium respectively.

The results for the ammonium and thallium salts of both acids and of the two series have also proved of great interest, and have thrown into prominent relief the important law governing the relations of the salts of metals of the same family group which has just been elucidated. For thallium is essentially different in its chemical nature from the family group of alkali metals—potassium, rubidium, and cæsium—being related to both the alkali group on the one hand, in the compounds in which thallium plays the part of a monad metal, and in which it may be said to replace the alkali metals ; and to the aluminium group on the other hand, in the compounds in which thallium acts as a triad. Ammonium also, while replacing potassium in a manner very similar to rubidium or cæsium, is obviously not in its constitution comparable with those metals, being a radicle group  $\text{NH}_4$  and not an element.

The results of the investigation of the ammonium double sulphates and selenates, which have now been completed as regards the two sets of groups containing respectively magnesium and zinc as the *M*-metals, are remarkably similar to those derived from the study of ammonium sulphate. Ammonium selenate has shown the different nature of the radicle ammonium as compared with the alkali metals very strikingly, by exhibiting dimorphism and preferring to crystallise commonly in its monoclinic rather than its second rhombic form, so that it cannot so directly enter into the comparison. The position of ammonium in the series, however, is much more clearly

shown in the monoclinic double salt series than in the rhombic simple salt series, ammonium selenate behaving just like the sulphate in readily forming these double salts with the selenates of the *M*-metals. Moreover, the rhombic salts exhibit exceedingly small differences in the angles between the external faces, the maximum observed between a potassium salt and a cæsium salt being only two-thirds of a degree, in exact measure 41' between potassium and cæsium sulphates and 40' between potassium and cæsium selenates; whereas the monoclinic double sulphates and selenates exhibit differences in the interfacial angles exceeding two degrees, the maximum observed between a potassium and a cæsium salt being 141', in the cases of potassium magnesium and cæsium magnesium sulphates. It might have been expected that the replacement of a so much greater integral part of the molecule as the alkali metal forms of the simple salt  $R_2\frac{S}{Se}O_4$  would be accompanied by a greater amount of angular change than when the same replacement occurs in the very much larger molecule of the double salt  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ , of which the alkali metal forms a much smaller integral part. But the question appears to be connected with the degree of symmetry; the higher the order of symmetry the smaller are the angular changes between the exterior faces, when one member of the family of metals or radicles forming the series of salts replaces another. This fact further emphasises the dominating influence of the alkali metal in determining the crystallographic properties of the salts, for very little effect, and that on no definite plan, accompanies the replacement of one *M*-metal in the double salt series by another, whereas, on the contrary, replacement of the alkali metal, or even of the sulphur by selenium, calls forth regular and considerable changes as we have seen.

It has been shown with respect to the three properties which refer to the fundamental structural unit of the crystals, namely, the molecular volume, the molecular distance ratios, and the molecular refraction (a measure of the molecular effect on the velocity of light transmission), that the ammonium salt of every group yet studied behaves almost exactly like the rubidium salt. This applies to both simple and double salts equally, and also to the case of ammonium selenate, in spite of the fact of its common form on which the constants were determined being the monoclinic one. If we could isolate absolutely pure crystals of the rhombic form (they have only yet been obtained as mixed crystals with other salts of the series) there is reason to believe the conformity would be even closer.

With respect to the crystallographic as distinct from the molecular-unit structural properties, they are found to be of two kinds. Those of the one kind follow the order of the molecular weights, in which case the ammonium salt stands first in the series. In this category come the densities, the rotation of the optical ellipsoid (in the cases of the monoclinic double salts), and the specific refraction and dispersion. Thus, while the whole of the properties of the crystals of the potassium, rubidium, and cæsium salts have been shown to be functions of the atomic weight of the alkali metal, and therefore of the molecular weight of the whole salt, only four properties obey a similar rule in the case of the ammonium salts, at once marking an essential difference between the ammonium complex and an alkali metal. As regards the properties of the other kind, which include the interfacial angles, the refractive indices and the axial ratios of the optical indicatrix which they determine, the mean refractive index for the whole crystal, and the double refraction, the ammonium salt of any group occupies a position varying somewhat in the different groups and in the two series, from one which

is quite close to the rubidium salt and just beyond it on the cæsium side, and represents the state of matters in the great majority of cases, to one which lies nearer to that of the cæsium salt, and represents the smaller number of cases. In the case of simple rhombic ammonium sulphate, the position near rubidium sulphate is occupied with respect to no fewer than nine different properties, including the mean refraction in the state of solution in water. Ammonium selenate, again in spite of its dimorphism, also follows this rule, by far the greater number of properties exhibiting it in the position just after rubidium selenate.

Hence it may be said that: *The general position of the ammonium salt of any group in either series, with respect to the large majority of the crystal properties, is quite close to the rubidium salt, just beyond it on the cæsium side.*

This somewhat surprising result as regards the position of the radicle  $\text{NH}_4$  group ammonium, has led the author to investigate whether the space-lattices of the ammonium salts are truly and strictly comparable with the space-lattices of the alkali-metallic salts. After a very full experimental enquiry it was concluded, on the ground of overwhelming evidence, not only from the author's own researches but from those of no fewer than three other independent workers, that they were indeed strictly comparable. For parallel growths and mixed crystals are produced with the greatest ease in the cases of the ammonium and rubidium salts of the same series and group, these salts being as we have seen, precisely those with very closely similar space-lattice constants, the molecular distance ratios. It is thus proved that: *The absolute as well as relative dimensions of the molecular unit cells of the space-lattices of the crystals of the rubidium and ammonium salts are almost identical, and thus adequately congruent for the crystals to grow*

*together in parallel growths and mixed crystals with the greatest ease.* Any supposition of a general expansion of the structure to admit the ammonium group of atoms is thus ruled out. For it has been definitely proved that when these structural constants—the molecular distance ratios—are very different, as is often the case with the two extreme members of a series, the potassium and caesium salts for instance, parallel growths and mixed crystals either do not form at all, or if they do, the crystals are invariably opaque and irregular. Thus this point of congruency, and therefore of strict comparability, of the ammonium and rubidium salts is conclusively proved.

The effect of this important fact is far reaching. For it means that the space-lattice assemblage must be sufficiently open to permit of the introduction of the eight additional atoms, which is the result of replacing two atoms of rubidium by two  $\text{NH}_4$  groups. Any theory of packing of the structural units which does not take account of this incontrovertible fact cannot, therefore, be expressing the whole truth.

*The position of thallium in the series is remarkably close to that of ammonium in everything except one very striking difference, which at once sets the thallium salts apart from the whole of the other salts of both series, namely, transcendent refractive power, that is, exceptionally great resistance to the vibration of light waves.* The refractive indices are higher than those of the caesium salts by an amount which is five times greater in the simple salt series than the amount by which those of the caesium salts are higher than those of the potassium salts. Not only is this outstanding prominence true of the specific refraction, but also in a lesser degree of the molecular refraction, that is, the power of resistance to light vibration exercised by the unit molecular cell of the space-lattice. *While thus differing so markedly in its optical properties, the molecular volumes and molecular*

*distance ratios of the thallium salts are almost identical with those of the analogous rubidium salts, just like the ammonium ones.* In respect to the interfacial angles, the differences from the potassium salt are nearly three times as much as when rubidium replaces potassium, and twice as much as when cæsium does so, the average changes, irrespective of direction, being proportional to the greater atomic weight of thallium. But the changes occur irregularly as regards their direction, so that the law of progression according to atomic weight does not apply, thallium, like ammonium, thus exhibiting its distinctive difference from the true alkali metals potassium, rubidium, and cæsium.

Thus, while the properties of the ammonium and thallium salts, both morphological and physical, are such as entitle them to be placed in the same two isomorphous series, as defined on page 124, they do not entitle them to places in the more exclusive eutropic series, as defined on page 125.

Hence the final conclusion as regards the ammonium and thallium salts may be stated in the following terms:—

*The thallium and ammonium salts of the two series of rhombic sulphates and selenates,  $R_2\frac{S}{Se}O_4$ , and monoclinic double sulphates and selenates,  $R_2M\left(\frac{S}{Se}O_4\right)_2 \cdot 6H_2O$ , exhibit properties fully entitling them to their inclusion in these respective series of isomorphous salts, understanding by the term "isomorphous series," a series the members of which bear a definite chemical analogy, crystallise with like symmetry, and develop forms the interfacial angles of which differ only by an amount which has not yet been observed to exceed  $2\frac{1}{2}$  degrees.*

*The more exclusive eutropic series within each of these isomorphous series, that is to say, the series in which the*

members exhibit the progression of the whole of the crystal properties according to the atomic weight of the interchangeable chemical elements, comprises solely the salts of the alkali metals potassium, rubidium, and caesium, which belong strictly to the same family group of the periodic classification, the thallium and ammonium salts being excluded by their essentially different chemical nature and their different crystallographic properties which follow therefrom.

One further general conclusion has been reached as the result of this work, embodying a fact which has been prominent throughout the whole course of the investigation, namely, that —

*Specific chemical substitutions are accompanied by definitely orientated changes in the crystal structure, indicating that particular chemical atoms occupy definitely localised positions in the chemical molecule, and therefore, as the molecule is the structural unit of the space-lattice, in the crystallographic structural unit.*

Thus it was proved that the replacement of one alkali metal by another in the rhombic series of sulphates and selenates invariably called forth predominating crystallographic changes in the direction of the vertical axis, while the substitution of selenium for sulphur brought about a preponderating amount of equatorial change. Similarly, in the monoclinic series of double salts, the replacement of the alkali metal was shown to affect chiefly the direction of the symmetry axis  $b$ , while the replacement of sulphur by selenium brought about dimensional change principally along the axis  $a$  lying in the symmetry plane. The establishment of the principle that each atom entering into a crystalline structure produces a definite and constant crystallographic effect, is probably one of the greatest advances which the investigation has resulted in.

It will be clear that the laws which have now been shown to govern the inter-relations of the members of

isomorphous series definitely allocate specific angles, crystal elements, structural dimensions of the molecular unit of the space-lattice, and physical properties to each individual member of an isomorphous series. The establishment of these laws thus at the same time removes the last and only possible supposed exceptions to the generalisation insisted on with so much persistence by Hauy, that every distinct chemical substance is endowed with a specific crystalline form peculiar to itself; and it defines in precise terms and explains the true meaning of Mitscherlich's principle of isomorphism, indicating the exact and limited sense in which it is correct, and to what extent the literal meaning of the word must be qualified.

In the long controversy between Hauy and Mitscherlich and their disciples we have one more instance, among the many presented by scientific progress, of two great master-minds regarding the same facts from two different points of view, and, through the medium of experimental data of only a crude and quite inadequate character, both arriving at what is broadly and for the main part the truth, but carrying their conclusions further than the data warranted, and so enveloping the truth and obscuring it by a cloud of error. This is now thus after many years swept away, and the precious kernel of truth brought to the clear light of day.

The achievement is another triumph for refined experimental method and laboriously careful and accurate measurement, before which in the long run no error can stand but must sooner or later be dissipated. The author has attempted to raise the accuracy of goniometrical measurements, made on carefully prepared materials of the highest purity, to the level on which atomic weight determinations stand to-day, and the measurement of the physical constants to the degree of accuracy of wave-length determinations by the inter-

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ference method, which are confessedly the two highest planes of accuracy and refinement to which the chemist and the physicist can respectively attain. How far he has succeeded it is for the reader to judge. But of this there can be no question, namely, that the author has had the privilege of reconciling and harmonising the work of Hauy and Mitscherlich, and of thus deciding finally the great controversy to which that work for many years gave rise. This alone is ample reward for the labours of twenty years. The research has been of the most deeply interesting, indeed fascinating, character throughout, and many rich rewards have come by the way in the shape of the most exquisite of all the phenomena which even Nature, ever so prodigal of her delights, can bestow.

real and of the utmost importance. They are so small in many cases that the older crude methods were quite incapable of detecting them, and the recent great progress has only been possible by the development of much more refined experimental methods and instruments. The only exceptions are in those cases where the symmetry reaches its maximum and the crystals belong to the cubic system, in which cases the symmetry itself determines the angles between the faces, and the crystals are geometrically strictly isomorphous. But even here, differences are revealed in their optical, thermal, elastic, and other physical properties.

Thirdly, it has been shown further that these small differences obey a most interesting law, which governs every property of the crystals, geometrical, structural, and physical ; namely, that they are functions of the atomic weights of the interchangeable chemical elements which give rise to the series.

Fourthly, we have learnt how to determine the relative dimensions of the unit of the crystal structure, the molecular cell, in these series of related compounds.

Fifthly, we have proved experimentally that the atoms of which the chemical molecule is composed,—corresponding to the molecular cell, the elementary parallelepipedon of the space lattice,—assume definite positions within the crystal and within the molecule. Also that the molecules are either similarly orientated,

the class, that is, to which of the thirty-two classes the crystal shall conform. Our former vague idea as to possible motion on the part of the atoms within the molecule when the substance is congealed into a crystal is thus dispelled, by this experimental fact; and that earlier view is now also profoundly modified by the discovery of the composite nature of the chemical atom—the unit of chemical combination as it is also the ultimate unit of crystal structure. For it is the component corpuscles which are in the state of organised motion, in regular accretions of cycles or groups as atomic weight rises, motion so rapid and powerful as to prevent intrusion within the boundaries of their sphere of motion, which are the confines of the atom. If, in addition to the intra-atomic corpuscular movements, the atom as a whole has a proper motion of its own within the molecule, for which there is no experimental evidence for the solid state, it is of so limited a character that its sphere of influence or range of motion occupies a definitely orientated part of the molecule, its radius being possibly a function of the temperature. The experimental facts are very clear in thus limiting any possible motion of the atom, and, indeed, also indicate that it is separated by an interspace from the other atoms of the molecule, or their spheres of influence.

Nothing is more important, among the most striking crystallographic advances of the past two decades, than this discovery of the fixed stereometric positions of the atoms or their spheres of influence in the molecule of the well ordered solid, the crystal. For not only does it at once explain why a particular class among the various classes possible to the system of symmetry in question is developed rather than another, but it also gives us the sanguine hope that it will prove the basis of a comprehensive understanding of the great and complicated question, what it is which determines a chemical substance to crystallise in a particular form.

Speculation is already rife, and the valency theory of Pope and Barlow,<sup>1</sup> and the interesting suggestions of Sollas,<sup>2</sup> are important instances of it. But all that has been stated in these pages is rigid fact, based on careful and irrefragable experiment and measurement. The author has always been very chary of speculation, feeling that the groundwork of facts, that is, of experimental data of the very highest authority and accuracy, needed consolidation and great augmentation before it could with advantage be built upon.

Chemists are at length realising, however, the undoubtedly vast importance which crystallography has for them, and to which they have been extraordinarily indifferent in the past, in spite of the remarkable nature of the experimental facts which have been revealed as regards the connection between crystalline form and chemical composition. Indeed, the value of crystallography, as the science of the organised and perfect solid, to both the chemist and the physicist can scarcely be overrated.

That the interest now happily awakened may be directed into the channel of further careful measurements and experimental work, on the part of a greatly increased number of investigators, is the hope of the author in writing this book, which attempts to give a faithful account of the mode in which the sure ground on which we stand to-day has been reached.

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<sup>1</sup> *Journ. Chem. Soc.*, 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528.  
Also *Annual Reports on the Progress of Chemistry*, 1908, p. 268.

<sup>2</sup> *Proc. Roy. Soc.*, 1898, **63**, 270, 286, and 296; 1901, **67**, 493.

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